

November 8, 2001

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U.S. Department of Energy
National Energy Technology Laboratory
PO Box 10940, MS 921-107
Pittsburgh, PA 15236-0940

Dear AAD Document Control:

Subject: Final Report for JV Task 24 – Investigation of the Fate of Mercury in a Coal
Combustion Plume Using a Static Plume Dilution Chamber
Cooperative Agreement No. DE-FC26-98FT40321; UND Fund 4727

Please find enclosed one copy of the final report for the subject project. A draft copy was submitted to the performance monitor on October 24, 2001. No changes were required; therefore, we are enclosing the final report with the Request for Patent Clearance for Release of Contracted Research Documents and the electronic copy.

If you have any questions regarding this submittal, please call me at (701) 777-5124, fax at (701) 777-5181, or e-mail at slandis@undeerc.org.

Sincerely,

Sheryl E. Landis
Manager, Contracts and Intellectual Property
Business and Operations

SEL/kmd

Enclosures

c/enc: Richard Read, NETL

JV TASK 24 – INVESTIGATION OF THE FATE OF MERCURY IN A COAL COMBUSTION PLUME USING A STATIC PLUME DILUTION CHAMBER

Final Report

(for the period February 17, 2001, through June 30, 2001)

Prepared for:

AAD Document Control

U.S. Department of Energy
National Energy Technology Laboratory
PO Box 10940, MS 921-107
Pittsburgh, PA 15236-0940

Cooperative Agreement No.: DE-FC26-98FT40321
Performance Monitor: Dr. Richard Read

Prepared by:

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November 8, 2001

Mr. James Kilgroe
U.S. Environmental Protection Agency
MD 65
86 T.W. Alexander Drive
Research Triangle Park, NC 27711

Dear Jim:

Subject: Final Report for JV Task 24 – Investigation of the Fate of Mercury in a Coal
Combustion Plume Using a Static Plume Dilution Chamber

Enclosed please find the final report for the subject task. Work on this project was performed at the University of North Dakota Energy & Environmental Research Center.

If you have questions or comments, I can be reached by phone at (701) 777-5138, by fax at (701) 777-5181, or by e-mail at dlaudal@undeerc.org.

Sincerely,

Dennis L. Laudal
Senior Research Advisor

DLL/kmd

Enclosures

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Energy & Environmental Research Center
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November 8, 2001

Mr. John Pavlish
Director, Center for Air Toxic Metals
Energy & Environmental Research Center
PO Box 9018
Grand Forks, ND 58202-9018

Dear John:

Subject: Final Report for JV Task 24 – Investigation of the Fate of Mercury in a Coal
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Enclosed please find the final report for the subject task. Work on this project was performed at the University of North Dakota Energy & Environmental Research Center.

If you have questions or comments, I can be reached by phone at (701) 777-5138, by fax at (701) 777-5181, or by e-mail at dlaudal@undeerc.org.

Sincerely,

Dennis L. Laudal
Senior Research Advisor

DLL/kmd

Enclosures

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Final Report

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Prepared for:

Mr. John Pavlish

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PO Box 9018
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U.S. DEPARTMENT OF ENERGY
National Energy Technology Laboratory

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1. Document Title: JV Task 24 B Investigation of the Fate of Mercury in a Coal Combustion Plume Using a Static Plume Dilution Chamber

2. Type of Document: ~ Technical Progress Report ~ Topical Report s Final Technical Report
~ Abstract ~ Technical Paper ~ Journal Article ~ Conference Presentation
~ Other (please specify): _____

3. Date clearance needed: _____

E4. Patent information

Yes No

~ s Is any patentable subject matter disclosed in the report?

~ ~ If so, has an invention disclosure been submitted to DOE Patent Counsel?

If yes, identify disclosure number or DOE Case Number _____

~ s Are there any patent-related objections to the release of this report? If so, state the objections.

E5. Signed _____ Date _____
(Contractor)

Name & Phone No. Sheryl E. Landis (701) 777-5124

Address Energy & Environmental Research Center, PO Box 9018, Grand Forks, ND 58202-9018

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ACKNOWLEDGMENT

This report was prepared with the support of the U.S. Department of Energy (DOE) National Energy Technology Laboratory, Cooperative Agreement No. DE-FC26-98FT40321. However, any opinions, findings, conclusions, or recommendations expressed herein are those of the author(s) and do not necessarily reflect the views of DOE.

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INVESTIGATION OF THE FATE OF MERCURY IN A COAL COMBUSTION PLUME USING A STATIC PLUME DILUTION CHAMBER

EXECUTIVE SUMMARY

Background

The 1990 Clean Air Act Amendments (CAAAAs) required the U.S. Environmental Protection Agency (EPA) to determine whether the presence of mercury in the stack emissions from fossil fuel-fired electric utility power plants poses an unacceptable public health risk. In December 2000, the EPA issued an intent to regulate for mercury from coal-fired boilers.

Mercury is emitted by both natural and human processes and cycles through atmospheric, aquatic, and terrestrial environments. The chemical form of mercury affects its transport through air, land, and water, as well as its chemical and biological behavior. Therefore, determination of speciation in a cooling coal combustion plume is important in estimating mercury fate and effects through atmosphere. However, little is known about the mercury transformations that occur in the plume. The mercury transformations that occur in the plume determine the rate and the form of mercury deposited in lakes and streams. Therefore, a logical step in mercury research is to apply what we know and extend this understanding slightly beyond the system to the plume region. Frontier Geosciences has developed a static plume dilution chamber (SPDC) that was designed to simulate plume conditions in the atmosphere. The SPDC is a 0.5-m³ chamber designed to simulate light and rain events and allow extensive mercury sampling as a function of time. A schematic of the SPDC is shown in Figure ES-1.

The SPDC has the potential to simulate plume and atmospheric effects on mercury that may help researchers understand the mercury chemistry in the plume. Based on previous results, this device has the potential to provide researchers with a relatively inexpensive and simple tool that can be used to study mercury transformations occurring just beyond energy conversion systems in the atmosphere in a simulated plume environment. Although the results at three field tests have demonstrated positive results, the SPDC needed to be tested under controlled conditions.

The Energy & Environmental Research Center (EERC), with help from Frontier Geosciences, conducted pilot-scale tests to more fully evaluate the SPDC under more controlled conditions than what occur at a full-scale system. This work was done in partnership with the U.S. Department of Energy (DOE), EPRI, and EPA through the EERC's Center for Air Toxic Metals (CATM).

Goals and Objectives

The overall goal of the project was to further develop and then verify SPDC's ability to determine the physical and chemical transformations of mercury in combustion stack plumes. Specific objectives of the project were to perform controlled tests at the pilot scale using dynamic

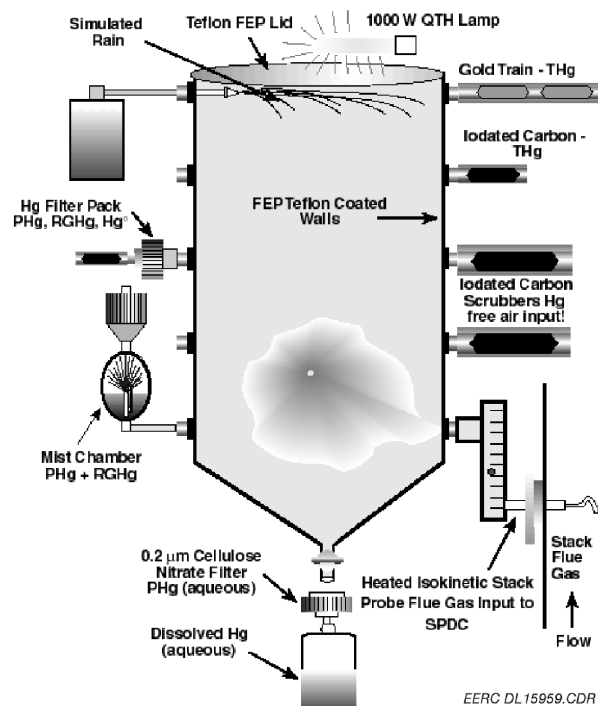


Figure ES-1. Schematic of the static plume dilution chamber.

spiking of known mercury compounds (i.e., Hg^0 and HgCl_2) to prove the ability of the SPDC to determine the following:

- Whether mercury condenses onto particulate matter in a cooling plume
- Whether there is reduction of Hg^{2+} to Hg^0 occurring in hygroscopic aerosols
- Whether condensed Hg^{2+} on particles is photochemically reduced to Hg^0
- Whether or not the Solid Ontario Hydro mercury speciation method (SOH) provides the same results as the Ontario Hydro (OH) mercury speciation method.

Approach

The overall test matrix is shown in Table ES-1. As can be seen in the table, the primary variables for the tests were particulate collection device (the level of particulate matter in the SPDC), mercury spiking, the use of light source, and the use of simulated rain. In addition, a test was completed to determine if ozone has an effect on the mercury speciation in the SPDC (Test 10). The coal chosen for the tests was a Blacksville eastern bituminous coal.

Table ES-1. Test Matrix^{a,b,c}

| Test No. | Fuel | Particulate Control Device | Hg Spike ^d | Light | Simulated Rain | Ozone, ppb |
|----------|-------------|----------------------------|-------------------------------------|-------|----------------|------------|
| 1 | Natural gas | Baghouse | Hg ⁰ | No | No | 0 |
| 2 | Natural gas | Baghouse | HgCl ₂ | No | No | 0 |
| 3 | Blacksville | ESP ^e | None | No | No | 0 |
| 4 | Blacksville | ESP | None | Yes | Yes | 0 |
| 5 | Blacksville | ESP | None | Yes | No | 0 |
| 6 | Blacksville | ESP | HgCl ₂ + Hg ⁰ | No | No | 0 |
| 7 | Blacksville | ESP | HgCl ₂ + Hg ⁰ | Yes | Yes | 0 |
| 8 | Blacksville | ESP | HgCl ₂ + Hg ⁰ | No | Yes | 0 |
| 9 | Blacksville | ESP | HgCl ₂ + Hg ⁰ | Yes | No | 0 |
| 10 | Blacksville | ESP | HgCl ₂ + Hg ⁰ | Yes | No | 200 |
| 11 | Blacksville | Baghouse | None | No | No | 0 |
| 12 | Blacksville | Baghouse | None | Yes | Yes | 0 |
| 13 | Blacksville | Baghouse | HgCl ₂ + Hg ⁰ | No | No | 0 |
| 14 | Blacksville | Baghouse | HgCl ₂ + Hg ⁰ | Yes | Yes | 0 |
| 15 | Blacksville | Baghouse | HgCl ₂ + Hg ⁰ | No | Yes | 0 |
| 16 | Blacksville | Baghouse | HgCl ₂ + Hg ⁰ | Yes | No | 0 |

^a The dilution ratio for the chamber was between 140:1 and 200:1 for all runs.

^b Hg⁰ was monitored continuously (every 3–5 minutes).

^c Hg²⁺ and particulate-bound mercury were sampled at 6, 30, 60, and 120 minutes for each test.

^d The HgCl₂ and Hg⁰ spikes were nominally 12 or 15 µg/dm³.

^e Electrostatic precipitator.

For each test, the speciated flue gas mercury was measured using the OH and the SOH methods. After a known volume of flue gas was injected into the SPDC, speciated vapor-phase mercury measurements were made as a function of time using a Tekran mercury continuous emission monitor (CEM) with a KCl denuder. The test was then conducted based on the test matrix shown in Table ES-1. Following each test, rinses were made of the unit, and the mercury was measured in the rinses.

Results

To ensure valid results, reasonable mercury balances were obtained around the SPDC. For purposes of these tests, mercury balances $\pm 25\%$ were considered reasonable. The balances were made based on the following:

- The mercury into the SPDC:
 - Mercury in the injected flue gas
 - Mercury in the dilution air (filtered ambient air)
 - Mercury in the sampling makeup air (filtered ambient air)
- The mercury out of the SPDC:
 - Mercury leaving the system as part of the sampling activities
 - Mercury remaining in the chamber at the end of the test
 - Mercury in the rinses.

Except for the first test on the natural gas, all the mercury balances were within acceptable limits.

The SPDC results show a very rapid decrease in both Hg^{2+} and particulate-bound mercury. It appears the rate of decrease is so fast that it occurs even before the first real measurement can be made. Two explanations are possible for the rapid decrease. First, the Hg^{2+} could have been reduced to Hg^0 ; secondly, the Hg^{2+} may have collected along the walls of the SPDC and been removed by the rinses. If there was a reduction of Hg^{2+} to Hg^0 , then a corresponding increase in Hg^0 should have been observed. In fact, there was a corresponding increase in Hg^0 for almost all the tests. However, the increase in the mass of Hg^0 is substantially less than the decrease in the mass of Hg^{2+} . Although it appears there is some reduction of Hg^{2+} to Hg^0 , there are also clearly substantial wall effects within the SPDC chamber. The overall change in Hg species within the SPDC chamber for each of the tests is shown in Table ES-2. An example of these results is shown graphically in Figure ES-2.

Table ES-2. Change in Mercury Species in the SPDC

| Test No. | Hg^{2+} Mass Change, ng | Hg^0 Mass Change, ng | Difference, ng |
|-----------------|--|---|-----------------------|
| 3 | 47.08 | 6.79 | 40.29 |
| 4 | 43.67 | 8.19 | 35.48 |
| 5 | 37.33 | 6.59 | 30.74 |
| 6 | 77.38 | 10.07 | 67.31 |
| 7 | 79.89 | 11.14 | 68.75 |
| 8 | 75.88 | 7.9 | 75.09 |
| 9 | 97.42 | 10.16 | 87.26 |
| 10 | 60.01 | 17.79 | 42.22 |
| 11 | 56.86 | -2.93 | 59.79 |
| 12 | 56.17 | 2.30 | 53.87 |
| 13 | 88.55 | 9.62 | 78.93 |
| 14 | 87.05 | 11.54 | 75.51 |
| 15 | 82.45 | 12.70 | 69.75 |
| 16 | 104.72 | 0.04 | 104.68 |

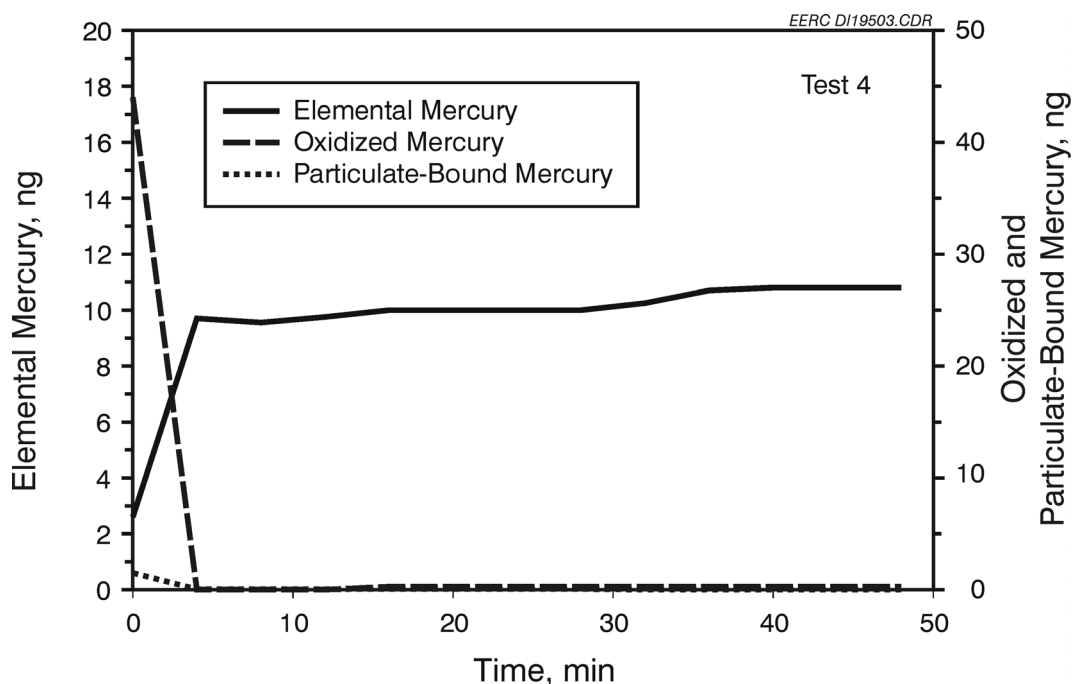


Figure ES-2. The change in mercury speciation as a function of time for SPDC Test 4.

As part of the SPDC testing, a comparison of the SOH method was made to the OH method sampling for speciated mercury. Paired sampling trains were run. The statistical comparison for each mercury species from the methods are shown in Table ES-3. In comparing the two methods, the calculated t-statistic is less than the t-value for each of the measured mercury species. Therefore, the two methods are statistically similar not only for total mercury but Hg^{2+} , Hg^0 , and particulate-bound mercury as well.

Table ES-3. Statistical Comparison between the OH and SOH Mercury Sampling Methods

| Statistical Component | Total Hg | Hg^0 | Hg^{2+} | Particulate-Bound Hg |
|------------------------------|----------|---------------|------------------|----------------------|
| Mean Difference, ng | 1.2500 | 0.2425 | 0.5188 | 0.6229 |
| Mean Standard Deviation, ng | 3.2490 | 1.0826 | 3.2486 | 1.1667 |
| Calculated t-statistic | 1.5390 | 1.4125 | 0.8958 | 0.6388 |
| t-statistic (95% confidence) | 1.7530 | 1.7530 | 1.7530 | 1.9430 |

Conclusions

Based on the SPDC tests, the following conclusions can be made:

- Good mass balances were obtained for the tests, $100 \pm 25\%$.

- The Hg^{2+} and the particulate-bound Hg decrease rapidly to at or near zero.
- For almost all tests, a rapid increase in Hg^0 occurred, however, the increase was not nearly to the degree that the Hg^{2+} and particulate bound-mercury decreased.
- The data appear to indicate that some reduction of Hg^{2+} to Hg^0 does take place in the SPDC (or plume?).
- The size of the SPDC (0.5 m^3) resulted in severe wall effects; a high percentage of the mercury goes to the wall to be removed later by the rinses.
- Because of the very rapid decrease in Hg^{2+} and the particulate-bound Hg, it was not possible to statistically evaluate the effects of light and rain on mercury chemistry in the SPDC.
- Because of the wall effects, a static SPDC is not a very useful tool in understanding mercury chemistry in combustion plumes. However, a dynamic system where flue gas is constantly flowing through the device and mixing with air may eliminate these effects.

Sampling Methodology

- The Tekran mercury CEM with KCl denuders appears to work well in speciating and measuring low levels of mercury.
- The SOH method statistically gives the same results as the OH mercury speciation method.

INVESTIGATION OF THE FATE OF MERCURY IN A COAL COMBUSTION PLUME USING A STATIC PLUME DILUTION CHAMBER

1.0 INTRODUCTION

The 1990 Clean Air Act Amendments (CAAAAs) required the U.S. Environmental Protection Agency (EPA) to determine whether the presence of mercury in the stack emissions from fossil fuel-fired electric utility power plants poses an unacceptable public health risk. EPA's conclusions and recommendations were presented in the *Mercury Study Report to Congress* (1) and the *Utility Air Toxics Report to Congress* (1). The first report addressed both the human health and environmental effects of anthropogenic mercury emissions, while the second addressed the risk to public health posed by the emission of mercury and other hazardous air pollutants from steam-electric generating units. Although these reports did not state that mercury controls on coal-fired electric power stations would be required, they did indicate that EPA views mercury as a potential threat to human health. In December 2000, the EPA did issue an intent to regulate for mercury from coal-fired boilers.

Mercury is emitted by both natural and human processes and cycles through atmospheric, aquatic, and terrestrial environments. Forms of mercury that appear most important in these environments are elemental mercury (Hg^0), inorganic or oxidized mercury (primarily Hg^{2+}), and methylmercury. The chemical form of mercury affects its transport through air, land, and water, as well as chemical and biological behavior. Elemental mercury is known to circulate in the atmosphere for about 1 to 2 years before it is deposited (2). Oxidized mercury in the atmosphere can be deposited directly to water bodies or transported from land by runoff and enter ponds, streams, rivers, lakes, etc. The water bodies contain microorganisms that have the metabolic capability to carry out chemical reactions that bind Hg^{2+} to methyl groups, producing methylmercury.

Although in-stack mercury speciation measurements are essential to develop and test control technologies and to provide data for input into atmospheric deposition models, the determination of speciation in a cooling coal combustion plume is more relevant for use in estimating mercury fate and effects. However, little is known about the mercury transformations that occur in the plume. The mercury transformations that occur in the plume determine the rate and the form of mercury deposited in lakes and streams. Although substantial research has been done in the past on mercury transformations within energy conversion systems—determining the concentrations of speciated mercury at the stack and doing ground-level atmospheric measurements—little has been done to determine the mercury chemistry, kinetics, and thermodynamics in the flue gas plume.

Therefore, a logical step in mercury research is to apply what we know to extend this understanding slightly beyond the system to the plume region. Frontier Geosciences has developed a static plume dilution chamber (SPDC) that was designed to simulate plume conditions in the atmosphere. The SPDC has the potential to simulate plume and atmospheric effects on mercury that may help researchers understand the mercury chemistry in the plume. Based on previous results, this device has the potential to provide researchers with a relatively inexpensive and simple tool that can be used to study mercury transformations occurring just beyond energy conversion systems in the

atmosphere in a simulated plume environment. Although the results at three field tests have demonstrated positive results (3), the SPDC needed to be tested under controlled conditions with mercury measurement methods that have been shown to correctly speciate mercury.

The Energy & Environmental Research Center (EERC), with help from Frontier Geosciences, conducted pilot-scale tests to more fully evaluate the SPDC under more controlled conditions than what occurs at a full-scale system. This work was done in partnership with the U.S. Department of Energy (DOE), EPRI, and EPA through the EERC's Center for Air Toxic Metals (CATM).

2.0 GOALS AND OBJECTIVES

The overall goal of the project was to further develop and then verify SPDC's ability to determine the physical and chemical transformations of mercury in combustion stack plumes. Specific objectives of the project were to perform controlled tests at the pilot scale using dynamic spiking of known mercury compounds (i.e., Hg^0 and HgCl_2) to prove the ability of the SPDC to determine the following:

- Whether mercury condenses onto particulate matter in a cooling plume
- Whether there is reduction of Hg^{2+} to Hg^0 occurring in hygroscopic aerosols
- Whether condensed Hg^{2+} on particles is photochemically reduced to Hg^0

3.0 FACILITY DESCRIPTION

3.1 Description of SPDC

The SPDC was a 1/2-cubic meter Teflon-coated reactor, as shown in Figure 1. Light was shone into the SPDC using a 1000-watt tungsten halogen quartz lamp. A total of ten ports with Teflon fittings allowed for plume input and sampling. The SPDC temperature was controlled by an insulated heating blanket. For these tests, the SPDC was maintained at a temperature of 300EF. A photograph of the unit is shown in Figure 2. It should be noted that the mist chambers shown in Figure 1 have been replaced with a Tekran mercury CEM (continuous emission monitor), KCl denuders, and a filter.

Prior to use, the SPDC is thoroughly cleaned, and fresh filter air is then pumped through the unit. After several complete exchanges of air, some of the air in the SPDC is evacuated until a negative pressure of about 5 psi is obtained. A known amount of flue gas is then introduced into the SPDC using a heated isokinetic sampling probe, as shown in Figure 1, for a set period of time (either 1 or 2 minutes). The flue gas in all cases was drawn from a location well downstream of the particulate control device.

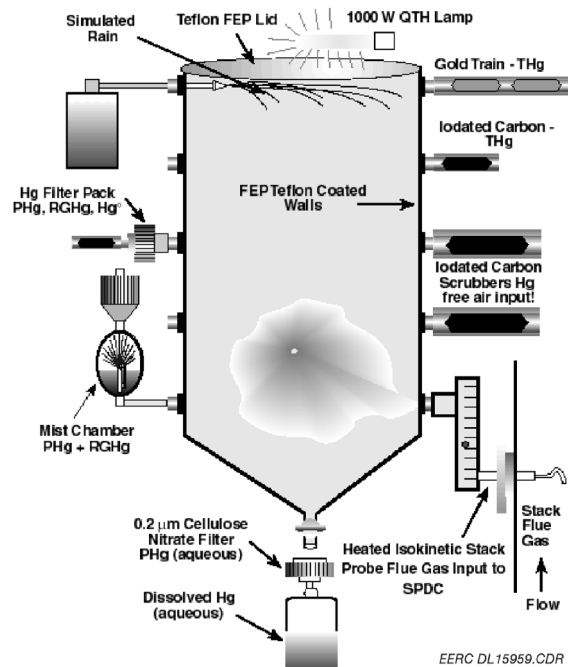


Figure 1. Schematic of the static plume dilution chamber (SPDC).



Figure 2. Photograph of the SPDC.

Following the injection of flue gas into the SPDC, filtered fresh air was allowed into the chamber until the SPDC was at an equilibrium with the ambient pressure. This resulted in good mixing of the flue gas in the chamber. The dilution of the flue gas with ambient air was to simulate plume dilution. The gas within the SPDC was allowed to react for a known amount of time (approximately 1 hour). The maximum dilution ratio depended on the incoming flue gas concentration, and although it could be as great as 500:1 (typical for a plume 5–10 km distant from the stack), for these tests, the dilution ratio was between 80 and 200 to 1.

After a predetermined aging time, a sample of the gas in the SPDC was withdrawn from three different locations and the mercury species measured using a Tekran mercury CEM system. For all samples, total mercury, Hg^{2+} , Hg^0 , and particulate-bound mercury were measured. Particulate-bound mercury and Hg^{2+} loss to the walls were recovered by pressure spray washing first with double-deionized water, then followed by 0.01%/3% v/v HCl/KCl solution. The wall wash was filtered in real time through a 0.2- μm cellulose nitrate filter. This allowed for the determination of both particulate and dissolved mercury in the aqueous phase.

Real-time rainwater washout simulation was done while the flue gas plume was introduced into the SPDC. For these tests simulated rainwater (10^{-9} molar H_2SO_4) was continuously sprayed into the SPDC falling through the plume. After a known amount of time, the rainwater was collected at the bottom of the SPDC and immediately filtered through 0.2- μm cellulose nitrate filters to separate dissolved versus particulate-bound mercury in the rainwater sample. The gas remaining in the SPDC was then sampled to determine Hg^0 , Hg^{2+} , particulate-bound mercury, and mercury wall loss.

3.2 Description of the Pilot-Scale Particulate Test Combustor (PTC)

The pilot-scale tests were conducted using the EERC PTC, with either an electrostatic precipitator (ESP) or a baghouse as the downstream particulate control device. This combustor has been extensively used by the EERC for a variety of work over the years, including tests to evaluate a catalytic fabric filter for NO_x reduction, projects to evaluate mercury measurement methods and control technologies, and projects for removing fine particulate matter. The following is a short description of the pilot-scale facilities.

The PTC is a 580-MJ/hr (550,000-Btu/hr) pulverized coal-fired unit designed to generate fly ash and flue gas chemistry representative of that produced in a full-scale utility boiler. Coal is introduced to the primary air stream via a screw feeder and ejector. An electric air preheater is used for precise control of the combustion air temperature. The PTC instrumentation permits system temperatures, pressures, flow rates, flue gas constituent concentrations, and ESP operating data to be monitored continuously and recorded on a data logger.

The PTC (shown in Figure 3) is designed to operate in conjunction with either an ESP or a fabric filter. The ESP is a single-wire, tubular ESP, with a specific collection area of 125 $\text{ft}^2/1000$ acfm (0.41 m^2/m^3) at 149EC (300EF) and a plate spacing of 27.9 cm (11 in.). Since the flue gas flow rate for the PTC is 3.67 scmm (130 scfm), the gas velocity through the ESP is

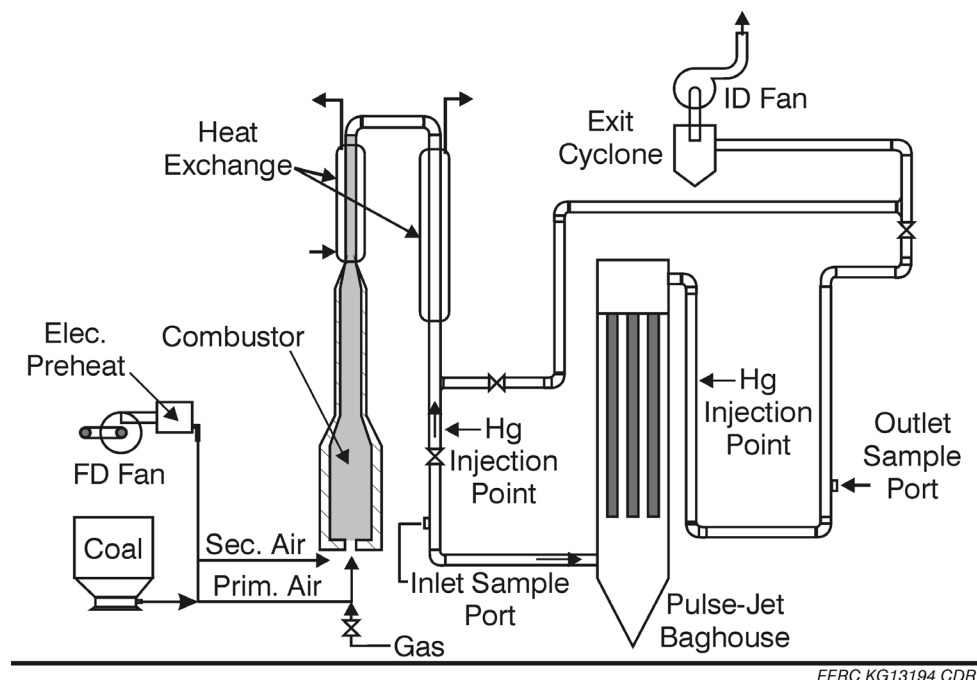


Figure 3. Schematic of the PTC.

1.5 m/min (5 ft/min). The ESP has an electrically isolated plate that is grounded through an ammeter, allowing continual monitoring of the actual plate current to ensure consistent operation of the ESP from test to test. A 0–100 kV (0–10 mA) power supply with sparking control is used to provide power to the ESP.

The pulse-jet baghouse used for these tests has a 0.508-m (20-in.) internal chamber that is heat-traced and insulated, with the flue gas introduced near the bottom. Three 3.96 m × 12.7 cm (13 ft × 5 in.) bags provide an air-to-cloth ration of 1.22 m/min (4 ft/min), based on typical flue gas production rate of 5.66 actual m³ (200 acfm) at 149EC (300EF). Each bag was cleaned separately with its own diaphragm pulse valve. So that difference in pressure drop for each test condition could be quantified, the bags were cleaned on a timed basis rather having the cleaning cycle be initiated by the pressure drop. Once bag cleaning was initiated, all three bags were pulsed in rapid succession on-line. The bags were composed of PTFE with GORE-TEX[®] expanded membrane.

3.3 Description of Sampling Procedures

As shown in Table 1, very extensive measurements were made on the device to determine total mercury, particulate-bound mercury, and gas-phase mercury (i.e., Hg⁰ and Hg²⁺). Included as one of the sampling methods was the newly developed solid sorbent Ontario Hydro method (SOH). This method was compared to the OH wet-chemistry method. The results comparing the OH and SOH method are discussed later in this report. The advantage of the solid sorbent method is simplicity and ease of use.

Table 1. Sampling Methods for SPDC and Flue Gas Mercury

| Method | Matrix | Measurement |
|--|-----------|--|
| Gold Traps | Plume air | Total Hg |
| Quartz Filter | Plume air | Particulate Hg |
| KCl Annular Denuder with Tekran | Plume air | Gas-phase Hg ²⁺ and total Hg |
| Tekran Mercury Analyzer ^a | Plume air | Total Hg |
| KCl Annular Denuder – Thermal Desorption into CVAFS ^b | Plume air | Gas-phase Hg ²⁺ |
| Quartz Filter Behind Denuder – Thermal Desorption into CVAFS | Plume air | Particulate-bound Hg |
| Deionized Water Rinse | Water | Surface loss |
| 3% KCl Rinse | Water | Surface loss |
| Simulated Rainwater (molar H ₂ SO ₄) | Water | Washout of particulate-bound Hg and gas-phase Hg ²⁺ |
| Cellulose Nitrate Filter | Water | Dissolved/particulate-bound Hg |
| Ontario Hydro Method | Flue gas | Hg ⁰ , Hg ²⁺ , and particulate-bound Hg |
| Solid Ontario Hydro Method (SOH) | Flue gas | Hg ⁰ , Hg ²⁺ , and particulate-bound Hg |
| Sorbent Ontario Hydro Method | Flue gas | Hg ⁰ and Hg ²⁺ |

^a Continuous emission monitor.

^b Cold-vapor atomic fluorescence spectroscopy.

3.3.1 The SOH Method

Because of the advantages of the SOH method for mercury speciation (including simplicity, no hazardous solutions, precision, sensitivity, accuracy, and cost), part of the scope of the project was to help validate the SOH method by intercomparing it to the accepted OH mercury speciation method. Flue gas measurements were made using both the Ontario Hydro method and the SOH, simultaneously.

The principle of the SOH method has been described previously in Prestbo and Bloom (4) and Prestbo and Tokos (5). It is a sampling method for mercury, which quantifies not only total mercury, but also the speciation between gas-phase Hg²⁺ and Hg⁰. It also identifies to some degree the fraction of mercury that is bound to particulate matter. The SOH sampling system employs a series of heated, solid-phase adsorbent traps to speciate mercury. In principle, flue gas Hg²⁺ is adsorbed by a KCl-impregnated quartz wool sorbent trap. Hg⁰ is collected by an iodated carbon sorbent after passing through the KCl/quartz sorbent.

In addition, the SOH method that was applied at the EERC collected samples using isokinetic principles. A miniparticulate filter consisting of a small quartz-fiber filter disk inserted into a quartz tube on a pure nickel support screen was used to collect fly ash to measure particulate-bound mercury (6). The analysis of the mercury on the fly ash was done using thermal desorption at 800EC (1472EF), passing through a heated MnO converter, gold preconcentration and, finally, measured using CVAFS detection.

3.3.2 Ontario Hydro Mercury Speciation Method

Speciated mercury analyses will be performed using the OH mercury speciation method, which is the method selected by EPA for its information collection request (ICR). A schematic of the sample train is shown in Figure 4. The development, testing, and verification of this method were done on the EERC PTC. The OH method is a modification of EPA Method 29 in which three aqueous 1 N KCl impinger solutions are substituted for one of the $\text{HNO}_3\text{--H}_2\text{O}_2$ solutions. The OH sampling method provides for the measurement of particulate-bound mercury and Hg^0 and Hg^{2+} concentration in the flue gas. The impinger solutions are analyzed for mercury by cold-vapor atomic absorption (CVAA) techniques. The analyses of the OH impinger solutions, reagent, field blanks, and field spikes will be done on-site. In this way, results are known within 24 hours, and changes to the test plan can be made while the sampling team is on-site. In addition, if problems do occur, corrective action can be taken and sampling redone, if necessary.

The OH method has been extensively tested at the EERC and has been shown to provide the best mercury speciation data for coal-fired boilers (7, 8). The method is currently being evaluated by American Society for Testing and Materials (ASTM) Subcommittee D22.03.01. A detailed

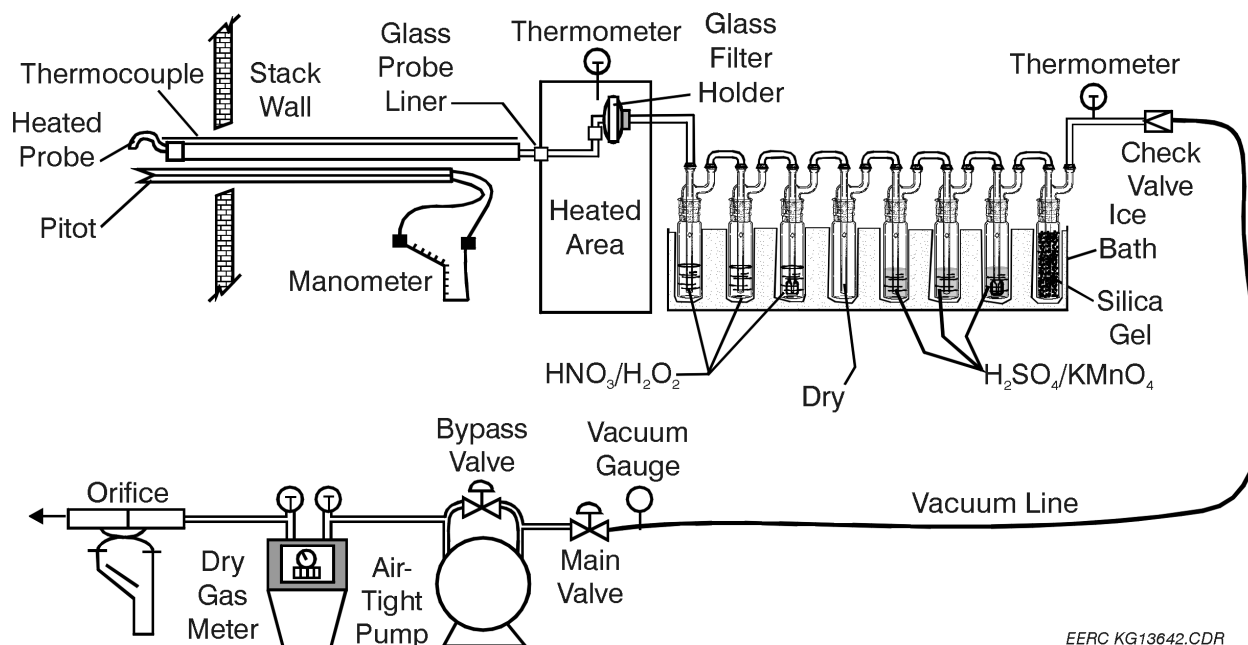


Figure 4. Schematic of the OH mercury speciation method.

description of the OH method in the ASTM format is available on the EPA Web site at <http://www.epa.gov/ttn/emc> under “Preliminary Methods.”

3.3.3 Tekran Mercury CEM

The mercury CEM used for these tests was the Tekran Model 2537A. The analyzer is based on the principle of atomic fluorescence (AF), which provides an inherently more sensitive signal than atomic absorption. The system uses a gold-impregnated silica support for preconcentrating the mercury and separating it from potential interferences that degrade sensitivity. The total time for the entire process is about 2.5 min. The analyzer is automated and has been used successfully for a number of years to measure ambient mercury. In addition, during the last 3 years, it has been used to measure mercury in flue gas streams from combustion systems. The system is calibrated using Hg^0 as the primary standard. The Hg^0 is contained in a closed vial, which is held in a thermostatic bath. The temperature of the mercury is monitored, and the amount of mercury is calculated using vapor pressure calculations. Typically, the calibration of the unit has proven stable over a 24-hr period. The Tekran CEM has a wide detection limit, from 0.1 ng/Nm³ to 50 µg/Nm³.

The instrument was originally designed to reliably measure ambient levels of vapor phase Hg^0 . A front-end sampler for the vapor-phase CEM instrument that differentiates between Hg^0 and Hg^{2+} has recently been developed. This was accomplished through the use of a programmable, temperature-regulated annular denuder coated with KCl that quantitatively removes vapor-phase Hg^{2+} from the air stream and does not collect Hg^0 . The Hg^0 is collected downstream and analyzed at 5-minute intervals in the conventional manner with the Tekran Model 2537A instrument. After a set period of time, zero air is passed through the denuder as it is rapidly heated. The accumulated Hg^{2+} is reduced to Hg^0 and moves to the analyzer where it is quantified. In this configuration, the Tekran instrument provides average concentrations of both Hg^0 and Hg^{2+} . The active length of the annular denuder is 23 cm. The denuder is constructed of quartz, with the active collection area modified to better support the KCl coating. Experiments thus far indicate the denuder needs to be recoated approximately once a month.

3.4 Mercury Spiking Systems

The tests required that known amounts of Hg^0 and Hg^{2+} be spiked into the flue gas stream. This was done using mercury-spiking systems previously developed at the EERC. These systems have been shown to accurately spike either Hg^0 or HgCl_2 into the PTC (7).

The spiking system for Hg^{2+} used mercury(II) chloride (HgCl_2) and is shown in Figure 5. As can be seen in Figure 5, the HgCl_2 is contained in three vessels on a fritted platform which allows N_2 to pass through. A mass flow controller is set at 35.6 cm³/min, which controls the amount of N_2 sweeping through the diffusion vessels. The dilution N_2 is preheated externally to 350EF (177EC) and kept at a constant flow rate of 20 scfh by using a flowmeter. The temperature of the oven is kept at 220EF (104EC).

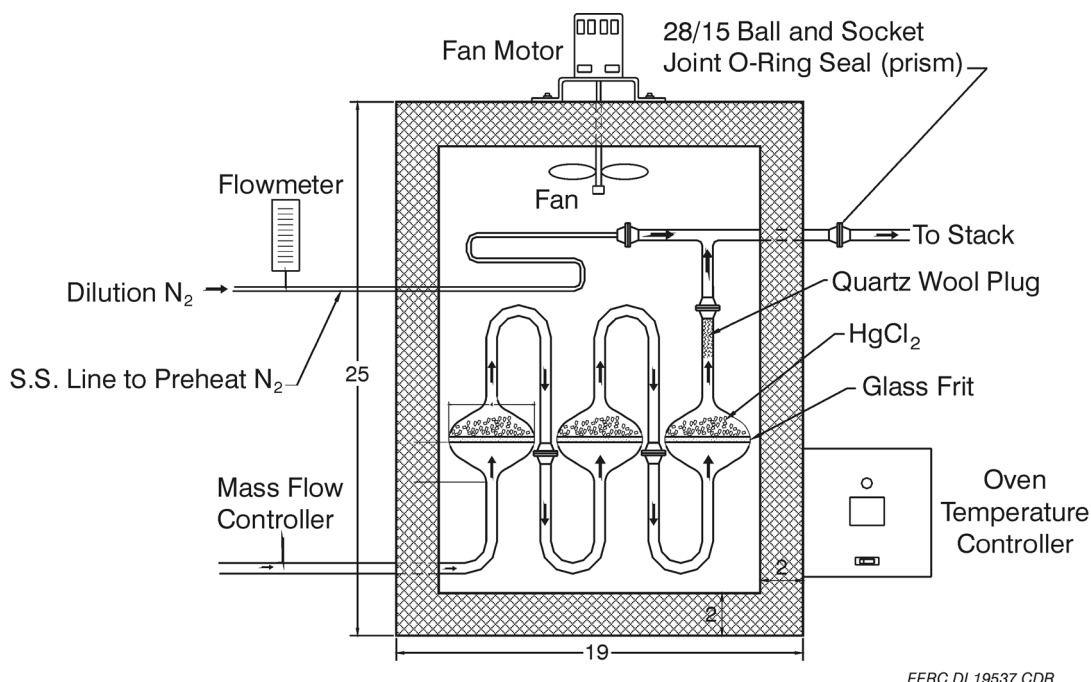


Figure 5. Schematic of the HgCl_2 spiking system.

The Hg^0 spiking system is shown in Figure 6. The Hg^0 is contained in a single diffusion vessel with three levels, allowing the N_2 to pass through. A mass flow controller is set at $34.0 \text{ cm}^3/\text{min}$, controlling the amount of N_2 sweeping the vessel. A dilution flow of N_2 is controlled by a flowmeter set at 20 scfh and preheated in the oven before it is mixed. The oven temperature is set at 84EC (184EF), and the injection arm is set at 160EC (320EF). Calibration curves for both systems are shown in Figures 7 and 8, and as can be seen in Figures 7 and 8, the mercury concentration exiting the spiking systems is linear with the amount of sweep gas.

4.0 APPROACH/WORK PLAN

The overall test matrix is shown in Table 2. As can be seen in the table, the primary variables for the tests were the particulate collection device (the level of particulate matter in the SPDC), mercury spiking, the use of light source, and the use of simulated rain. In addition, a test was completed to determine if ozone has an effect on the mercury speciation in the SPDC (Test 10). The coal chosen for the tests was a Blacksville eastern bituminous coal. A typical analysis of the coal is shown in Table 3. This coal was chosen for the project because of the extensive mercury research that has been done by the EERC, Consol, and others utilizing this coal. In addition, the EERC had enough of this coal on-site for the proposed tests; therefore, it was not necessary to purchase the coal.

The first two tests were conducted firing natural gas. The purpose of these tests was primarily shakedown. The shakedown was to ensure everything was working as intended both from the standpoint of the SPDC operation and the mercury-spiking systems.

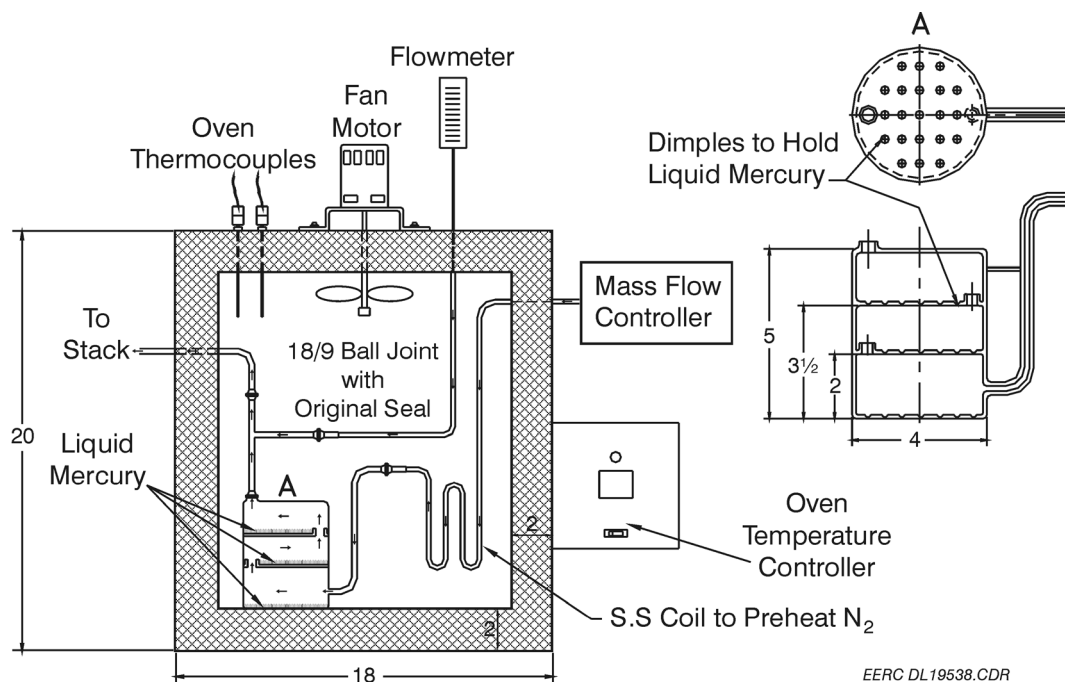


Figure 6. Schematic of the Hg⁰ spiking system.

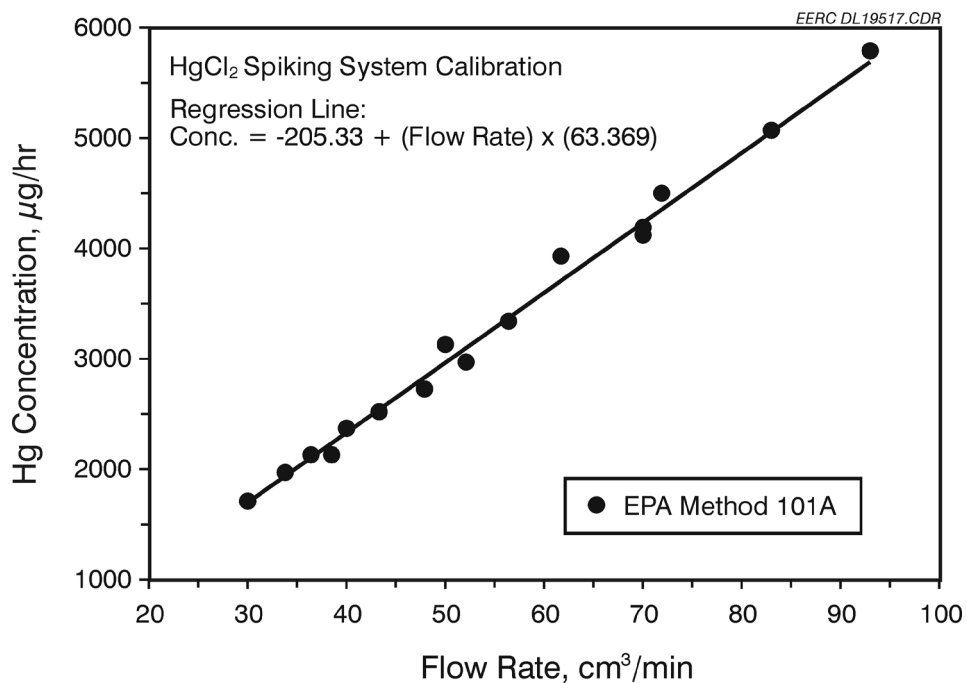


Figure 7. Calibration curve for the HgCl₂ spiking system.

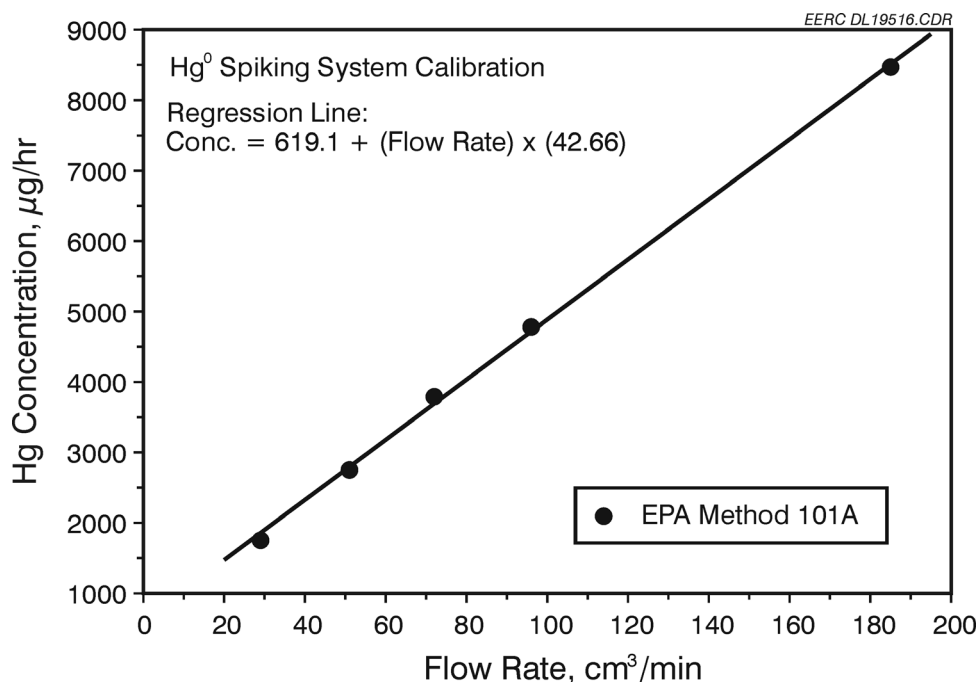


Figure 8. Calibration for Hg⁰ spiking system.

Following the two shakedown tests firing natural gas, Tests 3 through 10 (using the tubular ESP) were to determine if Hg²⁺ adheres to the particulate matter, reduced by light, or removed by simulated rain. It was expected that the ESP would remove about 95% of the particulate matter. The remaining tests (Tests 11 through 16) were conducted using a baghouse. The baghouse was expected to remove >99.5%. The baghouse tests were conducted to determine what the fate of the Hg²⁺ was in the SPDC when very little particulate matter is present. The baghouse test was conducted at the same conditions used for the ESP test.

5.0 OPERATIONAL PROCESS DATA

5.1 Particulate Test Combustor, Baghouse, and ESP

In general, the PTC operated well during the test. As shown in Table 4, the O₂ and SO₂ levels were relatively constant throughout the entire test program. However, the loss on ignition (LOI) was somewhat higher than in previous tests firing Blacksville coal. The LOI measurements were 13.64% for a sample collected from the ESP hopper and 9.08% for an ash sample collected in the baghouse hopper later in the test program. Typically, tests with Blacksville coal in the PTC resulted in LOI levels of about 3%–5% (9). The same two fly ash samples used to determine the percent LOI were also analyzed for mercury. The results showed that the concentration of mercury from the ESP

Table 2. Test Matrix ^{a,b,c}

| Test No. | Fuel | Particulate Control Device | Hg Spike ^d | Light | Simulated Rain | Ozone, ppb |
|----------|-------------|----------------------------|-------------------------------------|-------|----------------|------------|
| 1 | Natural gas | Baghouse | Hg ⁰ | No | No | 0 |
| 2 | Natural gas | Baghouse | HgCl ₂ | No | No | 0 |
| 3 | Blacksville | ESP | None | No | No | 0 |
| 4 | Blacksville | ESP | None | Yes | Yes | 0 |
| 5 | Blacksville | ESP | None | Yes | No | 0 |
| 6 | Blacksville | ESP | HgCl ₂ + Hg ⁰ | No | No | 0 |
| 7 | Blacksville | ESP | HgCl ₂ + Hg ⁰ | Yes | Yes | 0 |
| 8 | Blacksville | ESP | HgCl ₂ + Hg ⁰ | No | Yes | 0 |
| 9 | Blacksville | ESP | HgCl ₂ + Hg ⁰ | Yes | No | 0 |
| 10 | Blacksville | ESP | HgCl ₂ + Hg ⁰ | Yes | No | 200 |
| 11 | Blacksville | Baghouse | None | No | No | 0 |
| 12 | Blacksville | Baghouse | None | Yes | Yes | 0 |
| 13 | Blacksville | Baghouse | HgCl ₂ + Hg ⁰ | No | No | 0 |
| 14 | Blacksville | Baghouse | HgCl ₂ + Hg ⁰ | Yes | Yes | 0 |
| 15 | Blacksville | Baghouse | HgCl ₂ + Hg ⁰ | No | Yes | 0 |
| 16 | Blacksville | Baghouse | HgCl ₂ + Hg ⁰ | Yes | No | 0 |

^a The dilution ratio for the chamber was between 140:1 and 200:1 for all runs.

^b Hg⁰ was monitored continuously (every 3–5 minutes).

^c Hg²⁺ and particulate-bound mercury was sampled at 6, 30, 60, and 120 minutes for each test.

^d The HgCl₂ and Hg⁰ spikes were nominally 12 or 15 µg/dm³.

Table 3. Analysis of the Blacksville Coal

| | |
|---------------------------|--------|
| Mercury, ppm (dry) | 0.0916 |
| Chlorine, ppm (dry) | 758 |
| Proximate Analysis | |
| Moisture, % | 1.20 |
| Volatile Matter, % | 37.80 |
| Fixed Carbon, % | 53.30 |
| Ash, % | 7.71 |
| Ultimate Analysis | |
| Hydrogen, % | 4.62 |
| Carbon, % | 74.70 |
| Nitrogen, % | 2.09 |
| Sulfur, % | 2.03 |
| Oxygen, % | 7.65 |
| Heating Value, Btu/lb | 13,541 |

Table 4. PTC Operational Data^{1,2}

| Run No. | Date | Temp., ³ EF | SO ₂ ppm | CO ppm | CO ₂ % | O ₂ % | NO _x ppm |
|--------------------|-----------|---------------------------|------------------------|-----------|----------------------|---------------------|------------------------|
| 1 & 2 ⁴ | 3/7/2000 | 305 | 21 | 1.9 | 9.2 | 4.4 | 165 |
| | | | 23 | 0.1 | 1.0 | 1.2 | 6 |
| 3 | 3/8/2000 | 309 | 1216 | 6.5 | 14.0 | 5.1 | 603 |
| | | | 42 | 0.6 | 0.5 | 0.7 | 61 |
| 4 | 3/8/2000 | 310 | 1312 | 3.8 | 14.4 | 4.4 | 643 |
| | | | 19 | 0.2 | 0.2 | 0.3 | 18 |
| 5 | 3/10/2000 | 307 | 1386 | 3.9 | 13.9 | 1.4 | 633 |
| | | | 48 | 0.1 | 0.2 | 0.2 | 15 |
| 6 | 3/13/2000 | 310 | 1279 | 3.2 | 13.5 | 4.7 | 642 |
| | | | 43 | 0.8 | 0.7 | 0.5 | 21 |
| 7 | 3/13/2000 | 310 | 1205 | 6.6 | 13.1 | 5.4 | 678 |
| | | | 42 | 1.4 | 0.4 | 0.5 | 12 |
| 8 | 3/13/2000 | 305 | 1284 | 4.9 | 13.8 | 5.0 | 719 |
| | | | 46 | 0.8 | 0.6 | 0.6 | 27 |
| 9 | 3/14/2000 | 300 | 1240 | 2.6 | 13.7 | 5.4 | 690 |
| | | | 46 | 11.1 | 0.6 | 0.5 | 20 |
| 10 | 3/14/2000 | 305 | 1221 | 3.8 | 13.8 | 5.1 | 671 |
| | | | 65 | 1.1 | 0.7 | 1.0 | 33 |
| 11 | 3/15/2000 | 305 | 1251 | 2.0 | 13.4 | 5.8 | 664 |
| | | | 36 | 0.2 | 0.4 | 0.4 | 38 |
| 12 | 3/15/2000 | 301 | 1334 | 5.3 | 13.7 | 4.9 | 660 |
| | | | 43 | 0.5 | 0.4 | 0.5 | 26 |
| 13 | 3/16/2000 | 303 | 1329 | 1.6 | 13.8 | 5.1 | 646 |
| | | | 42 | 0.4 | 0.5 | 0.6 | 16 |
| 14 | 3/16/2000 | 302 | 1324 | 4.5 | 13.5 | 4.6 | 637 |
| | | | 37 | 0.2 | 0.4 | 0.4 | 16 |
| 15 | 3/16/2000 | 302 | 1290 | 3.3 | 14.6 | 4.9 | 670 |
| | | | 54 | 0.3 | 0.6 | 0.6 | 34 |
| 16 | 3/17/2000 | 300 | 1295 | 2.3 | 13.9 | 5.5 | 633 |
| | | | 47 | 0.7 | 0.6 | 0.5 | 18 |

¹ Each run is the average followed by the standard deviation.

² Data taken at the outlet of the particulate control device.

³ Temperature at the sampling location at the outlet of the ESP/baghouse. Sampling location was approximately 10 ft downstream of the control device.

⁴ Tests on natural gas (all others on coal).

and baghouse hoppers were 0.252 and 0.606 µg/g, respectively. This is exactly the same concentration in the ESP hopper ash that was obtained in a project using the PTC firing Blacksville coal when the LOI was only 3.22% (9), indicating that the higher LOI did not have much of an effect on the overall mercury results.

As indicated earlier, the ESP used for these tests was a single-wire pilot unit that was not very efficient. This was particularly true for Tests 9 and 10, where the ESP was severely sparking and the power supply was tripping out. An attempt was made to maintain the power supply at 50 kV; however, because of sparking problems, it was generally operated from 30 to 40 kV. For the baghouse tests, the pressure drop across was easily controlled. By using an on-line medium pressure-pulsing system, the pressure drop was controlled between 4 and 8 in. H₂O with a cleaning cycle of about 2 hours.

Using an average inlet dust loading of 1.404 grains/scf, Table 5 shows the particulate collection efficiency for all the tests both with the ESP and baghouse. It is clear from Table 5 that the particulate collection efficiency was much better when using the baghouse.

Table 5. Particulate Collection Efficiencies for the Tests

| Test No.* | Type of Particulate Collector | Outlet Dust Loading, gr/scf | Particulate Collection Efficiency, % |
|-----------|-------------------------------|-----------------------------|--------------------------------------|
| 3 | ESP | 0.3679 | 73.80 |
| 4 | ESP | 0.0737 | 94.75 |
| 5 | ESP | 0.0685 | 95.13 |
| 6 | ESP | 0.0590 | 95.80 |
| 7 | ESP | 0.0682 | 95.14 |
| 8 | ESP | 0.0921 | 93.44 |
| 9 | ESP | 0.9012 | 35.82 |
| 10 | ESP | 0.6633 | 52.77 |
| 11 | Baghouse | 0.0044 | 99.69 |
| 12 | Baghouse | 0.0043 | 99.70 |
| 13 | Baghouse | 0.0040 | 99.72 |
| 14 | Baghouse | 0.0105 | 99.25 |
| 15 | Baghouse | 0.0060 | 99.57 |
| 16 | Baghouse | 0.0114 | 99.19 |

* Tests 1 and 2 were with natural gas.

5.2 SPDC Operation

Once the system was set up and shakedown tests were completed to resolve some minor issues (primarily associated with applying a partial vacuum to the SPDC), the SPDC system worked as expected. It also appeared that the Tekran mercury CEM in conjunction with the KCl denuders worked well in providing speciated mercury results. Using this system eliminated the need for some

of the more difficult sampling methods, as used by Frontier Geosciences in the past, such as mist chambers and ion-exchange resins. The operational data for the SPDC for each of the tests are shown in Table 6.

6.0 RESULTS AND DISCUSSION

6.1 Mercury Balance

To ensure that the results are valid, reasonable mercury balances must be obtained around the SPDC. For purposes of these tests, mercury balances $\pm 25\%$ were considered reasonable. The components of the mercury balance into the SPDC are listed below:

- Mercury in the injected flue gas
- Mercury in the dilution air (filtered ambient air)
- Mercury in the sampling makeup air (filtered ambient air)

Table 6. SPDC Operational Conditions

| Run No. | SPDC Pressure, psi | Inlet Gas Temperature, EF | Sample Injection Time, min | Gas Flow Rate,* L/min | Dilution Ratio |
|---------|--------------------|---------------------------|----------------------------|-----------------------|----------------|
| 1 | ! 5.0 | 300 | 1 | 2.79 | 179.2 |
| 2 | ! 5.0 | 300 | 1 | 2.79 | 179.2 |
| 3 | ! 5.0 | 300 | 2 | 2.80 | 89.3 |
| 4 | ! 4.8 | 300 | 2 | 2.79 | 89.6 |
| 5 | ! 5.0 | 300 | 2 | 2.80 | 89.3 |
| 6 | ! 5.0 | 300 | 1 | 2.80 | 178.6 |
| 7 | ! 4.7 | 300 | 1 | 2.79 | 179.2 |
| 8 | ! 5.0 | 300 | 1 | 2.80 | 178.6 |
| 9 | ! 4.5 | 300 | 1.45 | 2.80 | 123.2 |
| 10 | ! 2.3 | 300 | 1 | 2.81 | 177.9 |
| 11 | ! 5.0 | 300 | 2 | 2.80 | 89.3 |
| 12 | ! 4.3 | 300 | 2 | 2.79 | 89.6 |
| 13 | ! 4.9 | 300 | 1 | 2.80 | 178.6 |
| 14 | ! 4.7 | 300 | 1 | 2.80 | 178.6 |
| 15 | ! 5.0 | 300 | 1 | 2.79 | 179.2 |
| 16 | ! 5.0 | 300 | 1 | 2.80 | 178.6 |

* The gas flow rate is defined at 21EC (70EF).

The mercury going into the SPDC must balance with the following components:

- Mercury leaving the system as part of the sampling activities
- Mercury remaining in the chamber at the end of the test
- Mercury in the rinses

The total mercury balance results are shown in Tables 7 and 8. The mercury concentration in the ambient air was measured to be 3 ng/m^3 . As can be seen, the balances were quite good as the results with just several exceptions were within $\pm 25\%$, indicating valid results.

6.2 Flue Gas Spiking

The spiking systems were tested in the first two natural gas tests. In the first test, a nominal $10 \text{ } \mu\text{g/Nm}^3 \text{ Hg}^0$ was spiked into the flue gas at the outlet of the ESP. The results showed that 98% was measured as Hg^0 . In Test 2, $10 \text{ } \mu\text{g/Nm}^3 \text{ HgCl}_2$ was spiked into the system's flue gas at the outlet of the ESP. The results for this test showed about 80% was measured as Hg^{2+} and 20% as Hg^0 , indicating some reduction occurred. For the coal tests, nominally $12 \text{ } \mu\text{g/Nm}^3$ of each species was spiked into the flue gas. Averaging the baseline mercury measurements (Tests 4, 5, 11, and 12) gives a baseline total mercury concentration of 9.35 ± 1.47 . Using this value, the spiking results (Tests 6–9 and Tests 10–16) are shown in Table 9. From these data, it appears that for Tests 13 to 15, the mercury spiking was closer to $15 \text{ } \mu\text{g/Nm}^3$ each.

Table 7. Total Mercury Balance Data

| SPDC Run No. | Hg In | | | Hg Out | | |
|--------------------|-------------------------------|-----------------------------|------------------------------------|---------------------------------|---------------------------------|-----------------------|
| | Hg-Injected Flue Gas ng | Hg in Dilution Air ng | Hg in Sampling Makeup Air ng | Hg in SPDC End of Test ng | Hg Removed by Sampling ng | Hg in Rinses ng |
| 1 | 28.7 | 0.94 | 0.17 | 37.79 | 4.08 | 3.29 |
| 2 | 29.1 | 0.94 | 0.14 | 11.67 | 1.04 | 12.44 |
| 3 | 56.3 | 0.94 | 0.10 | 10.71 | 0.69 | 25.44 |
| 4 | 48.0 | 0.93 | 0.16 | 11.08 | 1.08 | 29.58 |
| 5 | 42.8 | 0.93 | 0.20 | 9.82 | 1.33 | 34.64 |
| 6 | 96.2 | 0.94 | 0.18 | 25.31 | 3.29 | 56.00 |
| 7 | 100.0 | 0.94 | 0.18 | 27.64 | 4.02 | 48.59 |
| 8 | 99.2 | 0.94 | 0.18 | 27.37 | 3.21 | 43.47 |
| 9 | 130.9 | 0.94 | 0.18 | 14.70 | 2.13 | 91.03 |
| 10 | 90.6 | 0.94 | 0.18 | 22.83 | 3.00 | 64.94 |
| 11 | 59.9 | 0.93 | 0.18 | 0.79 | 3.00 | 43.74 |
| 12 | 58.3 | 0.93 | 0.18 | 5.95 | 0.66 | 36.41 |
| 13 | 112.9 | 0.94 | 0.18 | 31.32 | 3.71 | 69.29 |
| 14 | 112.8 | 0.94 | 0.18 | 34.42 | 3.97 | 41.58 |
| 15 | 108.7 | 0.94 | 0.18 | 35.94 | 4.17 | 46.37 |
| 16 | 130.5 | 0.94 | 0.18 | 24.08 | 2.84 | 88.14 |

Table 8. Total Mercury Balance

| SPDC Run No. | Total Hg in to SPDC, ng | Total Hg out of SPDC, ng | Mercury Balance (out/in) % |
|-----------------------------|--|---|---|
| 1 | 29.82 | 47.70 | 160.0 |
| 2 | 30.16 | 27.70 | 91.8 |
| 3 | 57.37 | 39.39 | 68.7 |
| 4 | 49.08 | 46.18 | 94.1 |
| 5 | 43.97 | 48.34 | 109.9 |
| 6 | 97.34 | 87.15 | 89.5 |
| 7 | 101.12 | 84.70 | 83.8 |
| 8 | 100.33 | 78.50 | 78.2 |
| 9 | 132.05 | 110.40 | 83.6 |
| 10 | 91.74 | 93.31 | 101.7 |
| 11 | 61.04 | 47.37 | 77.6 |
| 12 | 59.37 | 47.46 | 79.9 |
| 13 | 114.02 | 106.87 | 93.7 |
| 14 | 113.88 | 84.41 | 74.1 |
| 15 | 109.85 | 90.92 | 82.8 |
| 16 | 131.66 | 117.60 | 89.3 |

Table 9. Mercury Spiking Results

| SPDC Run No. | Total Hg, $\mu\text{g}/\text{Nm}^3$ | Baseline Hg $\mu\text{g}/\text{Nm}^3$ | Amount Hg Spiked $\mu\text{g}/\text{Nm}^3$ |
|-----------------------------|---|---|--|
| 6 | 34.37 | 9.35 | 25.02 |
| 7 | 35.84 | 9.35 | 26.49 |
| 8 | 35.43 | 9.35 | 26.08 |
| 9 | 32.25 | 9.35 | 22.90 |
| 10 | 32.26 | 9.35 | 22.91 |
| 13 | 40.32 | 9.35 | 30.97 |
| 14 | 40.27 | 9.35 | 30.92 |
| 15 | 38.97 | 9.35 | 28.62 |
| 16 | 46.62 | 9.35 | 37.27 |

6.3 Flue Gas Mercury Speciation

The mercury speciation results using the OH method are shown in Table 10. Based on the volume of flue gas sampled, the expected mass loading to the SPDC for each of the mercury species was then calculated. The flue gas results for the baseline tests (Tests 3 and 11) are typical for tests at the outlet of the particulate collection device firing Blacksville coal in the PTC (8). As would be

Table 10. Speciated Mercury Measured in the Flue Gas and Expected Loading to the SPDC

| SPDC Run | Mercury Concentration in Flue Gas | | | | Volume Flue Gas Injected to SPDC, L | Expected Mercury Loading to SPDC from Flue Gas | | | |
|----------|-------------------------------------|---|--|---|-------------------------------------|--|--------------------|-----------------------|--------------------|
| | Total Hg, $\mu\text{g}/\text{Nm}^3$ | Hg^0 , $\mu\text{g}/\text{Nm}^3$ | Hg^{2+} , $\mu\text{g}/\text{Nm}^3$ | Hg_p , $\mu\text{g}/\text{Nm}^3$ | | Total Hg, ng | Hg^0 , ng | Hg^{2+} , ng | Hg_p , ng |
| 1 | 10.29 | 10.05 | 0.23 | 0.02 | 2.79 | 28.7 | 28.0 | 0.6 | 0.1 |
| 2 | 10.42 | 2.11 | 8.30 | 0.01 | 2.79 | 29.1 | 5.9 | 23.2 | 0.0 |
| 3 | 10.06 | 0.54 | 8.68 | 1.70 | 5.60 | 56.3 | 3.0 | 48.6 | 9.5 |
| 4 | 8.60 | 0.46 | 7.88 | 0.26 | 5.58 | 48.0 | 2.6 | 44.0 | 1.5 |
| 5 | 7.65 | 0.46 | 6.81 | 0.38 | 5.60 | 42.8 | 2.6 | 38.1 | 2.1 |
| 6 | 34.37 | 5.85 | 27.96 | 0.57 | 2.80 | 96.2 | 16.4 | 78.3 | 1.6 |
| 7 | 35.84 | 6.81 | 28.73 | 0.30 | 2.79 | 100.0 | 19.0 | 80.2 | 0.8 |
| 8 | 35.43 | 7.61 | 27.19 | 0.63 | 2.80 | 99.2 | 21.3 | 76.1 | 1.8 |
| 9 | 32.25 | 1.26 | 24.10 | 6.89 | 4.06 | 130.9 | 5.1 | 97.8 | 28.0 |
| 10 | 32.26 | 1.72 | 21.65 | 8.89 | 2.81 | 90.6 | 4.8 | 60.8 | 25.0 |
| 11 | 10.70 | 0.44 | 10.23 | 0.04 | 5.60 | 59.9 | 2.5 | 57.3 | 0.2 |
| 12 | 10.44 | 0.36 | 10.07 | 0.01 | 5.58 | 58.3 | 2.0 | 56.2 | 0.1 |
| 13 | 40.32 | 8.45 | 31.85 | 0.02 | 2.80 | 112.9 | 23.7 | 89.2 | 0.1 |
| 14 | 40.27 | 9.12 | 31.14 | 0.02 | 2.80 | 112.8 | 25.5 | 87.2 | 0.1 |
| 15 | 38.97 | 9.38 | 29.56 | 0.04 | 2.79 | 108.7 | 26.2 | 82.5 | 0.1 |
| 16 | 46.62 | 8.91 | 37.69 | 0.02 | 2.80 | 130.5 | 24.9 | 105.5 | 0.1 |

expected, because of the higher particulate collection efficiency, less particulate-bound mercury was in the outlet flue gas for the baghouse test compared to the ESP tests. This result was substantiated by the lower concentration of mercury in the ESP hopper ash compared to the baghouse, 0.252 and 0.606 $\mu\text{g}/\text{g}$, respectively. It should also be noted that although equal amounts of Hg^0 and Hg^{2+} were spiked into the flue gas, there was substantial oxidation of the Hg^0 to Hg^{2+} . This has also been observed in previous tests (8).

6.4 SPDC Results

The SPDC mercury speciation results for each of the 14 tests (excluding the two natural gas tests) are shown in Figures 9 through 22. These figure show the vapor-phase mercury speciation as a function of time within the SPDC chamber. It is assumed that at time zero, the total amount of Hg^{2+} and particulate-bound mercury is the amount expected (from Table 10) based on the flue gas mercury speciation measurements. For the calculations incorporated into the graphs in Figures 9 through 22, it is assumed that all of the mercury in the dilution and makeup air is Hg^0 . It can be seen, in all of the figures, that there is a very rapid decrease in both Hg^{2+} and particulate-bound mercury. It appears that the rate of decrease is so fast that it occurs even before the first real measurement can be made. The overall change in Hg^{2+} mass within the SPDC chamber for each of the tests is shown in Table 11. There are two possible explanations for the rapid decrease. First, the Hg^{2+} could have been reduced to Hg^0 , and secondly, the Hg^{2+} may have collected along the walls of the SPDC and been removed

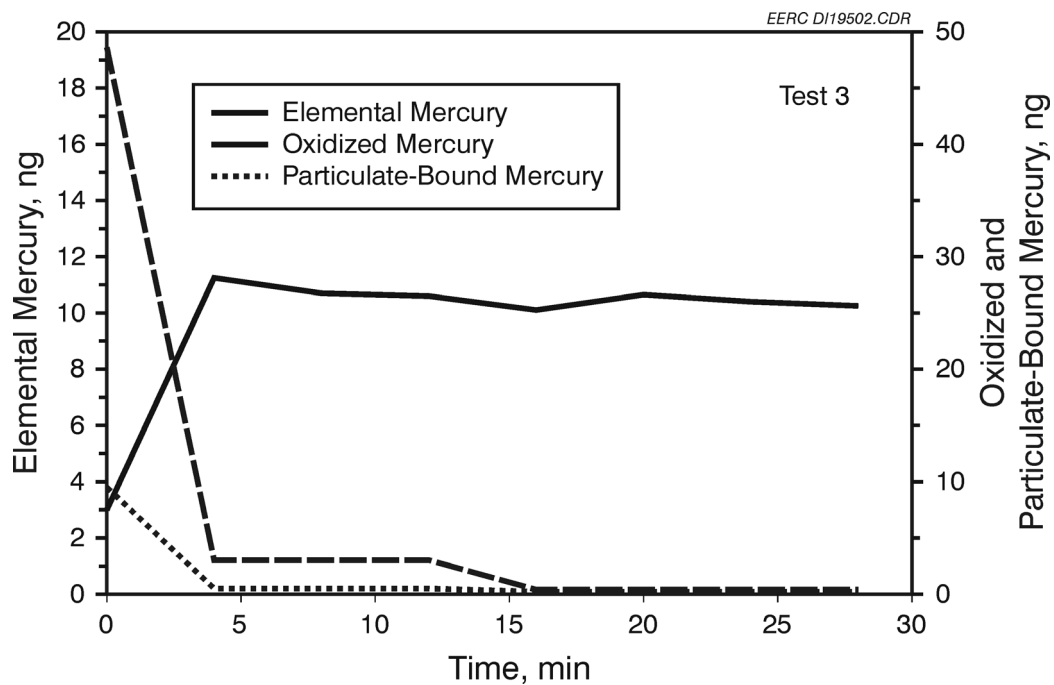


Figure 9. The change in mercury speciation as a function of time for SPDC Test 3.

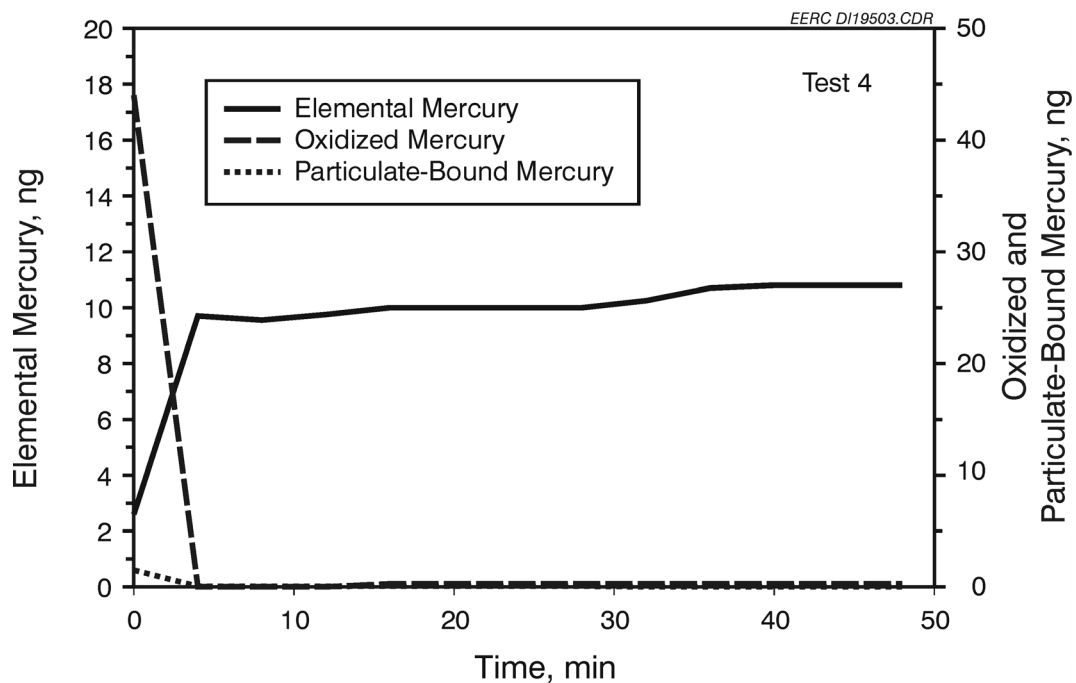


Figure 10. The change in mercury speciation as a function of time for SPDC Test 4.

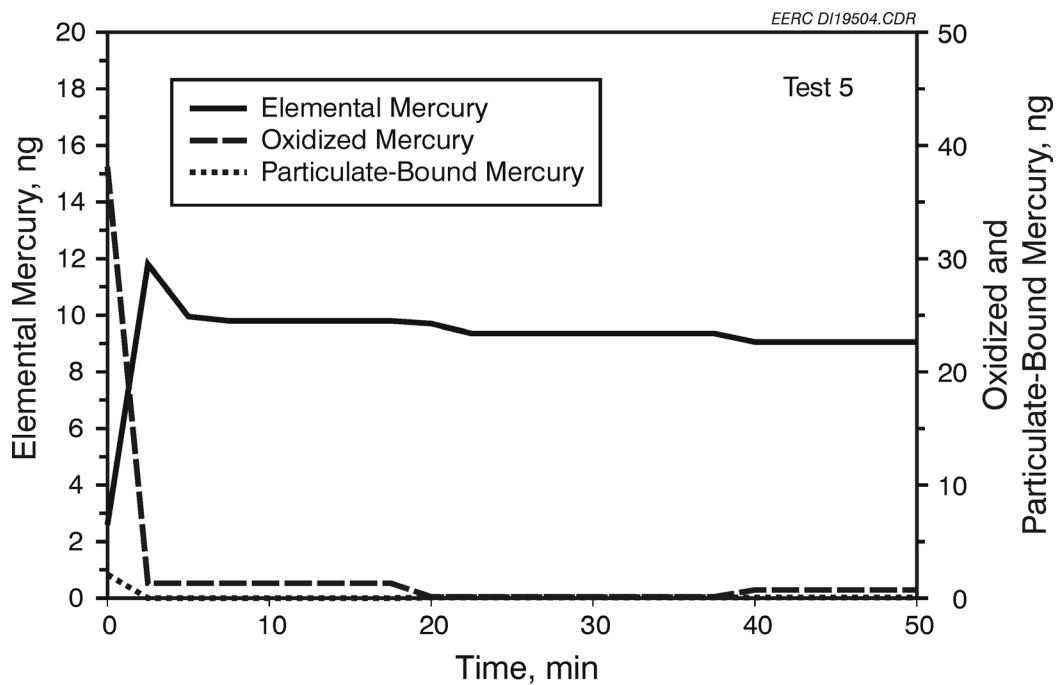


Figure 11. The change in mercury speciation as a function of time for SPDC Test 5.

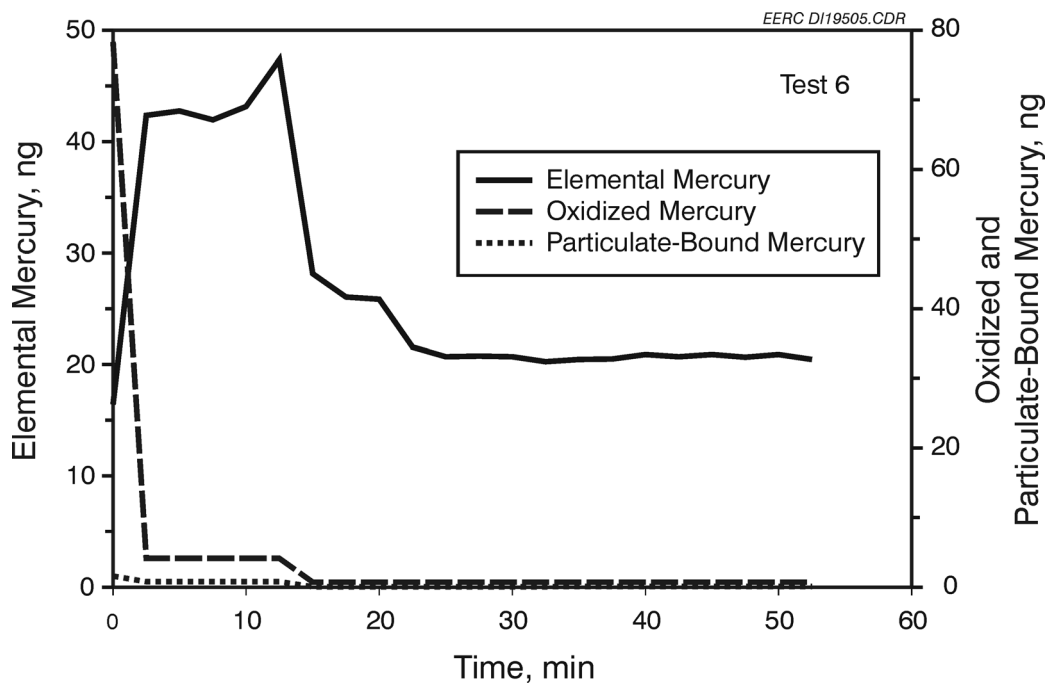


Figure 12. The change in mercury speciation as a function of time for SPDC Test 6.

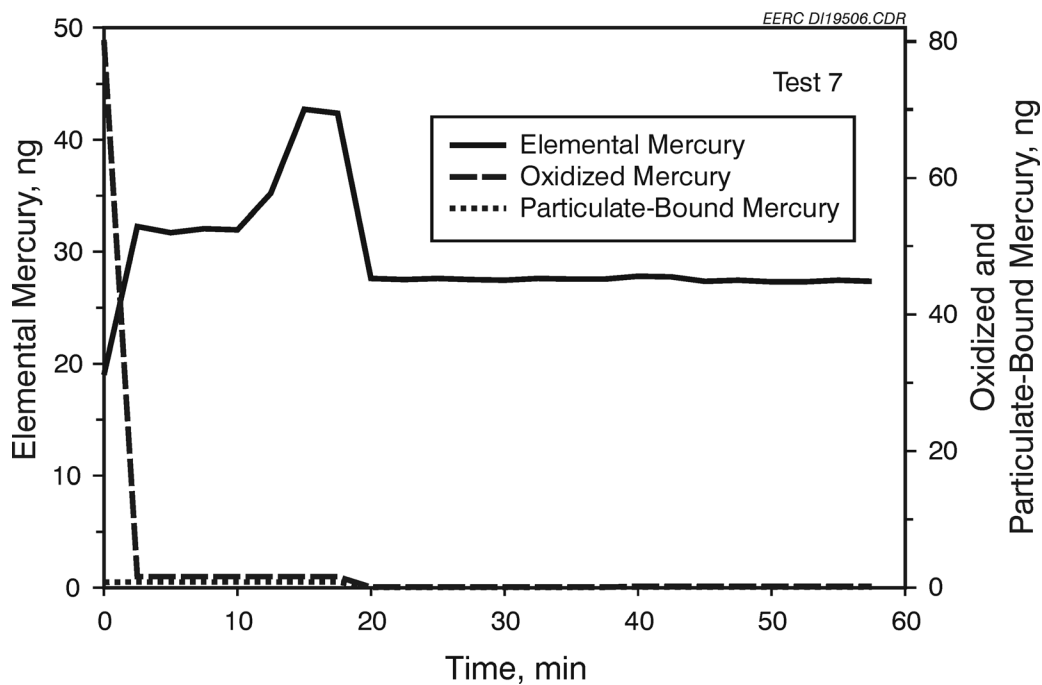


Figure 13. The change in mercury speciation as a function of time for SPDC Test 7.

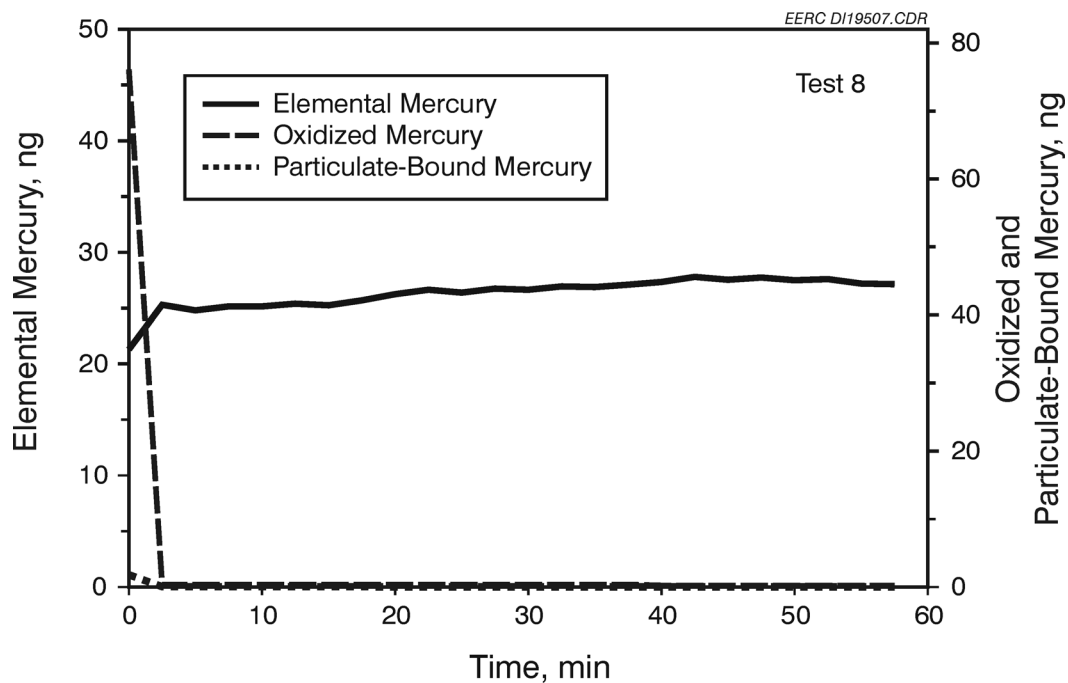


Figure 14. The change in mercury speciation as a function of time for SPDC Test 8.

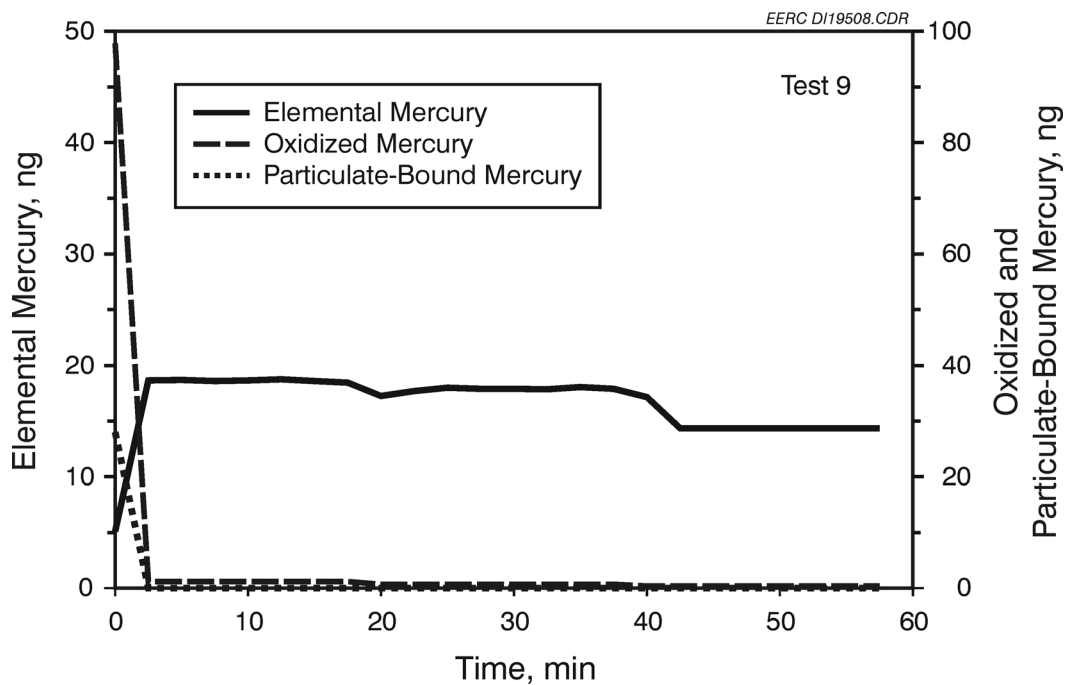


Figure 15. The change in mercury speciation as a function of time for SPDC Test 9.

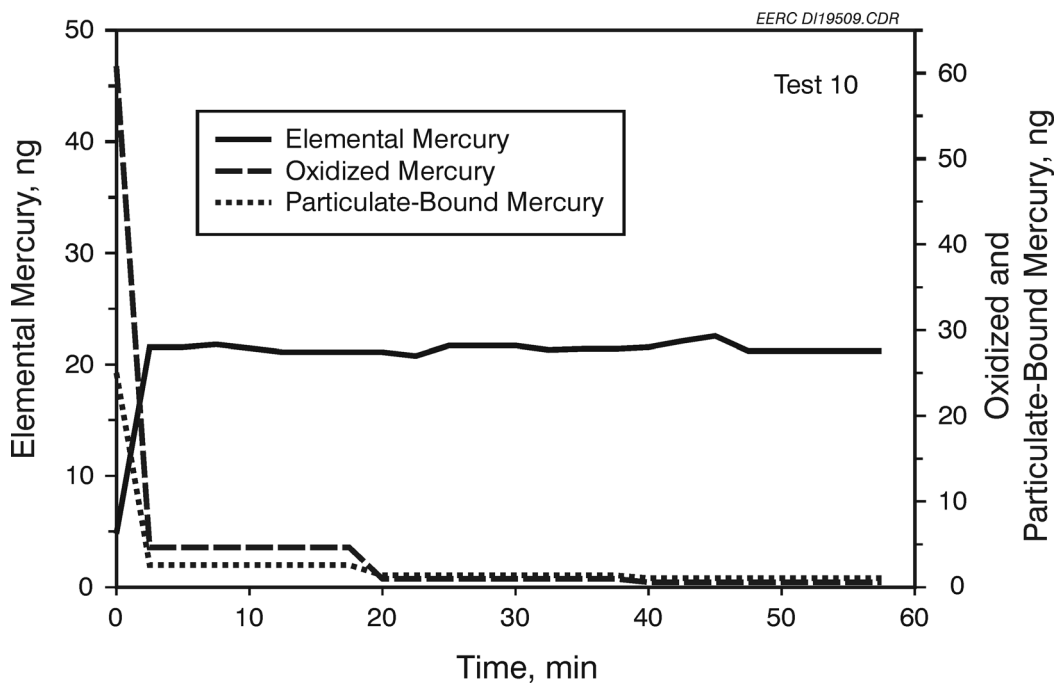


Figure 16. The change in mercury speciation as a function of time for SPDC Test 10.

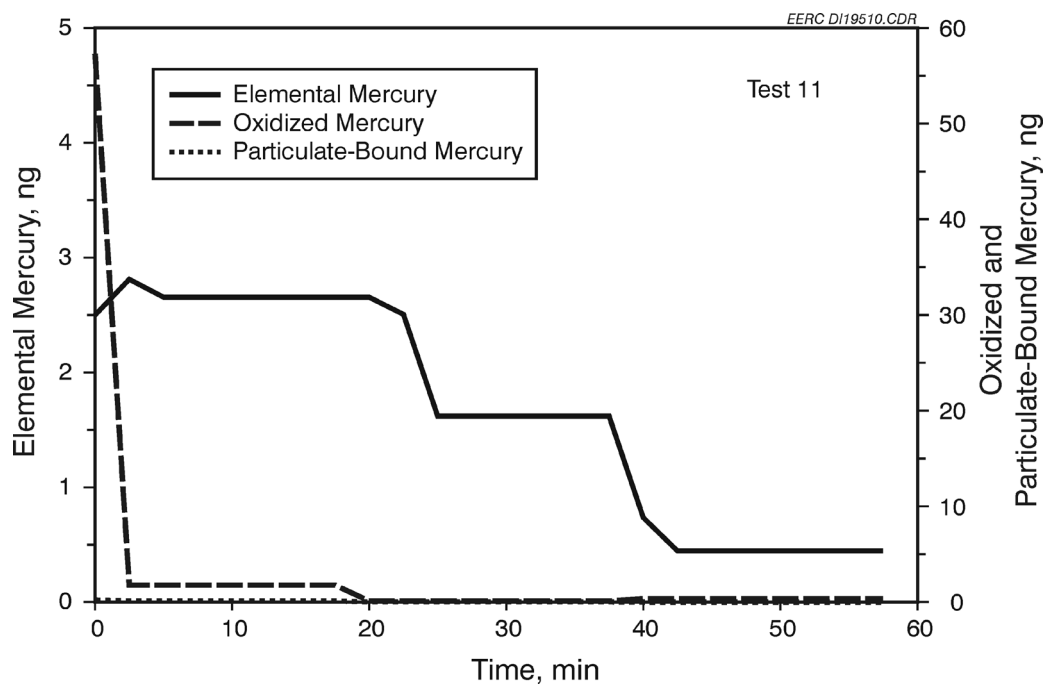


Figure 17. The change in mercury speciation as a function of time for SPDC Test 11.

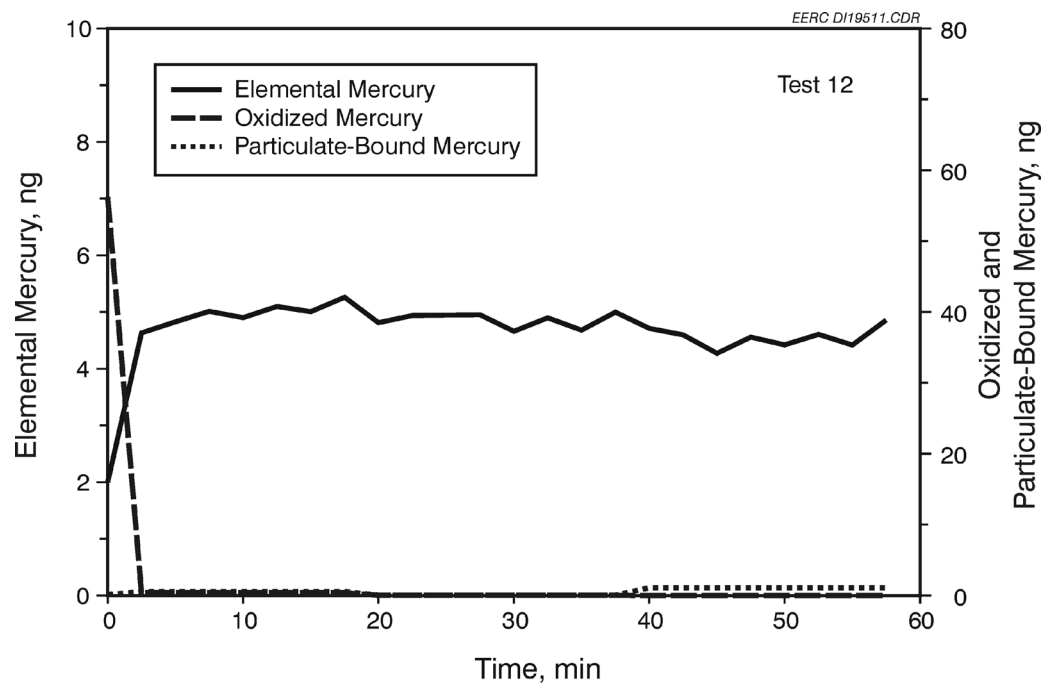


Figure 18. The change in mercury speciation as a function of time for SPDC Test 12.

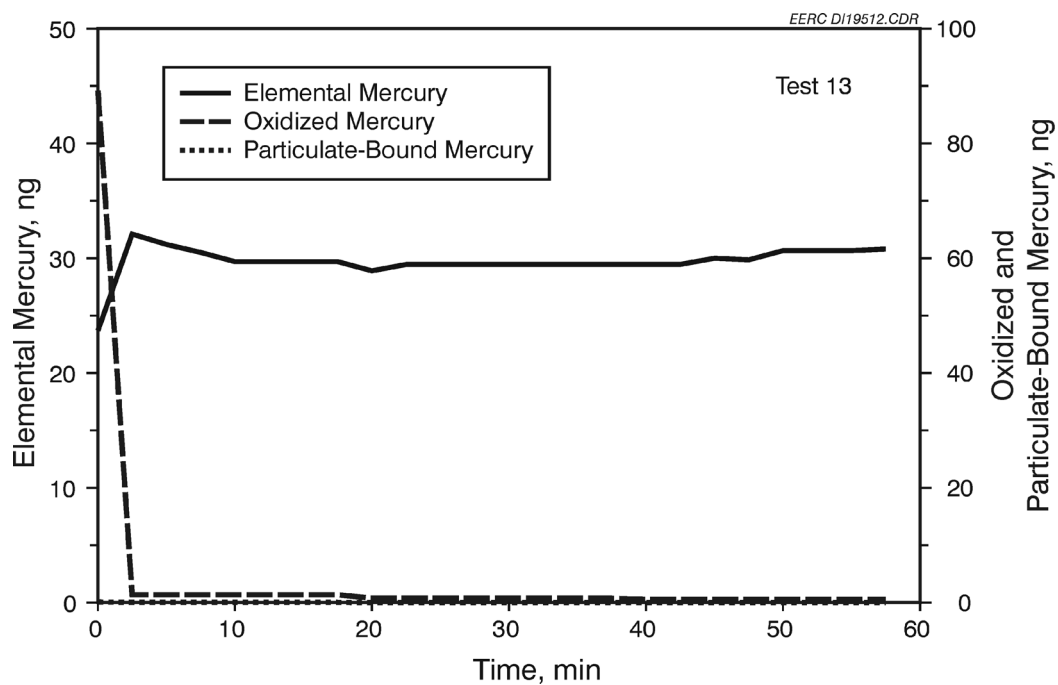


Figure 19. The change in mercury speciation as a function of time for SPDC Test 13.

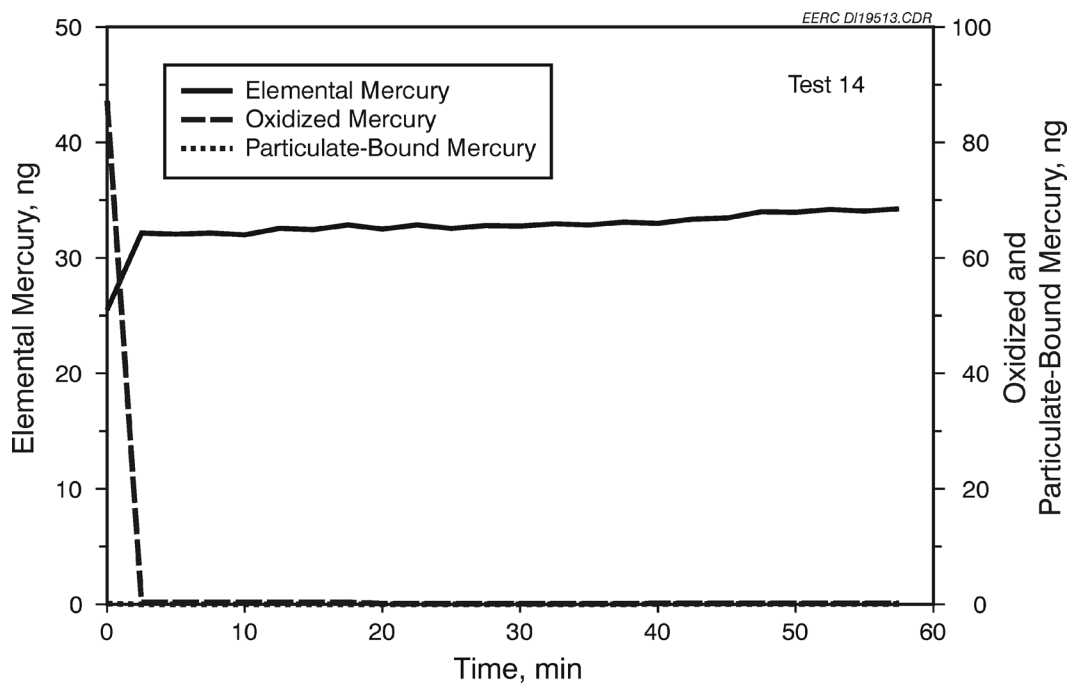


Figure 20. The change in mercury speciation as a function of time for SPDC Test 14.

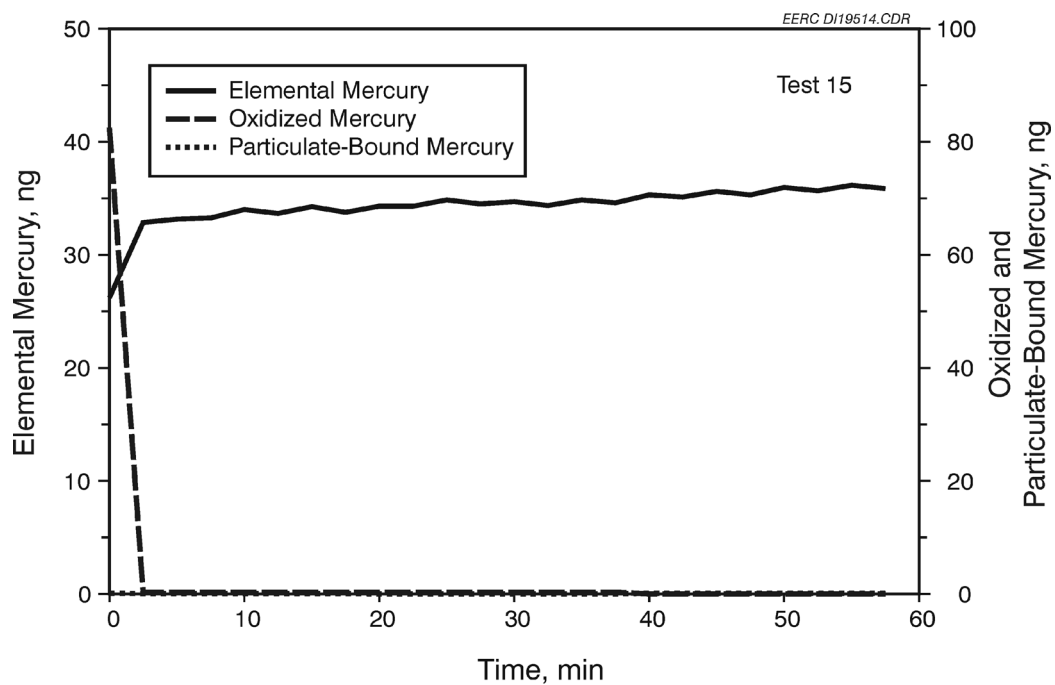


Figure 21. The change in mercury speciation as a function of time for SPDC Test 15.

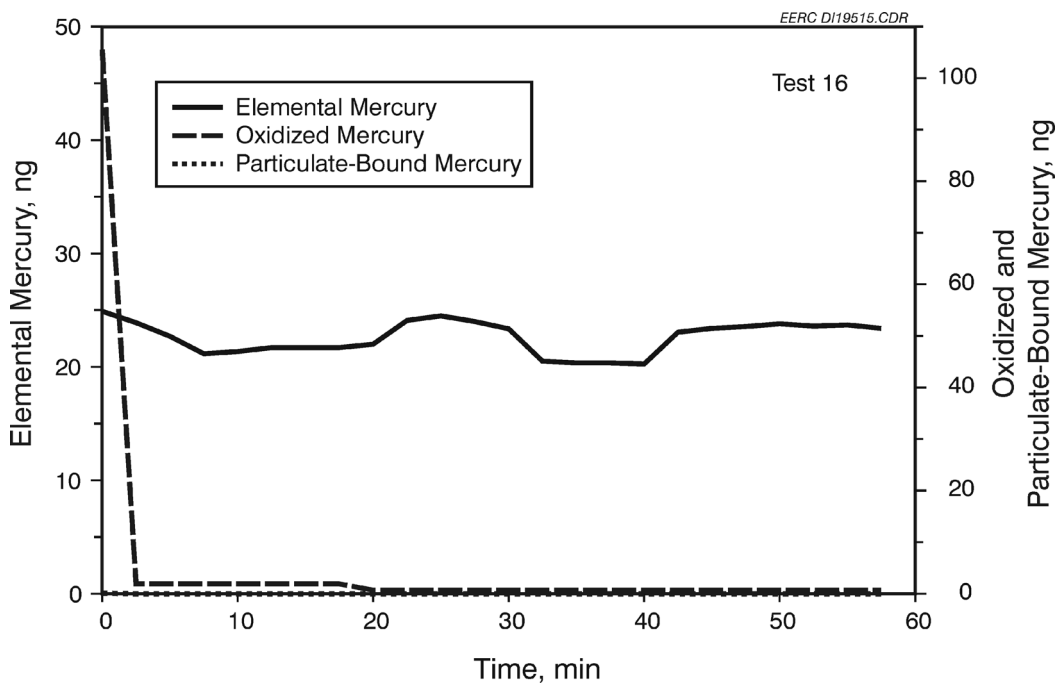


Figure 22. The change in mercury speciation as a function of time for SPDC Test 16.

Table 11. Overall Change in SPDC Vapor-Phase Oxidized Mercury

| SPDC Run | Hg²⁺ in Flue Gas, ng | Hg²⁺ Gas Sampled, ng | Hg²⁺ in Chamber, ng | Hg²⁺ Total, ng | Hg²⁺ Mass Change, ng |
|-----------------|--|--|---------------------------------------|----------------------------------|--|
| 3 | 48.61 | 0.08 | 0.25 | 0.33 | 47.28 |
| 4 | 43.97 | 0.02 | 0.28 | 0.30 | 43.67 |
| 5 | 38.14 | 0.09 | 0.72 | 0.81 | 37.33 |
| 6 | 78.29 | 0.20 | 0.71 | 0.91 | 77.38 |
| 7 | 80.16 | 0.08 | 0.20 | 0.28 | 79.89 |
| 8 | 76.13 | 0.04 | 0.22 | 0.25 | 75.88 |
| 9 | 97.85 | 0.09 | 0.35 | 0.43 | 97.42 |
| 10 | 60.84 | 0.25 | 0.58 | 0.83 | 60.01 |
| 11 | 57.29 | 0.09 | 0.34 | 0.43 | 56.86 |
| 12 | 56.19 | 0.02 | 0.00 | 0.02 | 56.17 |
| 13 | 89.18 | 0.11 | 0.52 | 0.63 | 88.55 |
| 14 | 87.19 | 0.02 | 0.12 | 0.14 | 87.05 |
| 15 | 82.47 | 0.02 | 0.00 | 0.02 | 82.45 |
| 16 | 105.53 | 0.13 | 0.68 | 0.81 | 104.72 |

by the rinses. If there was a reduction of Hg²⁺ to Hg⁰, then a corresponding increase in Hg⁰ should have been observed.

In fact, there was a corresponding increase in Hg⁰ for almost all of the tests, as shown in Table 12. However, the increase in the mass of Hg⁰ is substantially less than the decrease in mass of Hg²⁺. Although it appears there is some reduction of Hg²⁺ to Hg⁰, there are also clearly substantial wall effects within the SPDC chamber. As shown by the good mercury balances, the mercury that is attracted to the walls of the SPDC are removed in the rinses of the chamber conducted at the end of each test. It is interesting to note that the percentage of mercury in the rinses measured at the end of the test was relatively constant from test to test. The average was 67%, with a standard deviation of only 12%.

Unfortunately, because of the very rapid changes that occurred in the SPDC, it is not possible to do a statistical evaluation to determine if the variables (light, simulated rain, ozone) had an effect on mercury speciation. Simply looking at the figures and the data, it appears that simulated rain does result in a more thorough removal of the Hg²⁺ and particulate-bound mercury as they become zero almost immediately. The addition of ozone (Test 10) did show a very high level of particulate-bound mercury in the flue gas following the ESP. However, for this test, the ESP was not operating at peak efficiency, and the dust loading was much higher than in previous tests. The same situation existed for Test 9 without ozone, and that test also showed much higher particulate-bound mercury. Therefore, it is not possible to make any conclusions as to the effect of ozone. The measurements made around the SPDC are shown in Appendix A.

Table 12. Hg⁰ Mass Balance for SPDC Tests

| SPDC Run No. | Hg ⁰ In | | | | Hg ⁰ Out | | | Hg ⁰ Mass Change, ng |
|--------------------|------------------------------------|--------------------------------------|--|---------------------------------|---------------------------------------|-----------------------------------|---------------------------------|---------------------------------------|
| | Hg ⁰ Flue Gas, ng | Hg ⁰ Makeup Air, ng | Hg ⁰ Dilution Air, ng | Hg ⁰ Total, ng | Hg ⁰ gas Sampled, ng | Hg ⁰ Chamber, ng | Hg ⁰ Total, ng | |
| 3 | 3.02 | 0.10 | 0.94 | 4.06 | 0.59 | 10.25 | 10.84 | 6.79 |
| 4 | 2.57 | 0.16 | 0.94 | 3.66 | 1.05 | 10.80 | 11.85 | 8.19 |
| 5 | 2.58 | 0.20 | 0.94 | 3.71 | 1.24 | 9.05 | 10.29 | 6.59 |
| 6 | 16.38 | 0.17 | 0.94 | 17.49 | 3.05 | 24.50 | 27.55 | 10.07 |
| 7 | 19.00 | 0.18 | 0.94 | 20.12 | 3.91 | 27.35 | 31.26 | 11.14 |
| 8 | 21.31 | 0.18 | 0.94 | 22.43 | 3.18 | 27.15 | 30.33 | 7.90 |
| 9 | 5.12 | 0.18 | 0.94 | 6.24 | 2.04 | 14.35 | 16.39 | 10.16 |
| 10 | 4.83 | 0.18 | 0.94 | 5.96 | 2.55 | 21.20 | 23.75 | 17.79 |
| 11 | 2.46 | 0.18 | 0.94 | 3.58 | 0.20 | 0.44 | 0.65 | ! 2.93 |
| 12 | 2.01 | 0.18 | 0.94 | 3.13 | 0.57 | 4.86 | 5.43 | 2.30 |
| 13 | 23.66 | 0.18 | 0.94 | 24.78 | 3.60 | 30.80 | 34.40 | 9.62 |
| 14 | 25.54 | 0.18 | 0.94 | 26.66 | 3.95 | 34.25 | 38.20 | 11.54 |
| 15 | 26.17 | 0.18 | 0.94 | 27.29 | 4.14 | 35.85 | 39.99 | 12.70 |
| 16 | 24.95 | 0.18 | 0.94 | 26.07 | 2.71 | 23.40 | 26.11 | 0.04 |

6.5 Comparison of the SOH Method to the Ontario Hydro Method

As part of the SPDC testing, a comparison of the SOH method was made to the OH method sampling for speciated mercury. Paired sampling trains were run. The results of the sampling are shown in Table 13 along with the statistical comparison for each mercury species. For the two methods, the calculated t-statistic is less than the t-value for each of the measured mercury species. Therefore, the two methods are statistically similar not only for total mercury but Hg²⁺, Hg⁰, and particulate-bound mercury as well. The draft final report completed by Frontier Geosciences comparing the two methods is found in Appendix B.

7.0 QUALITY CONTROL

The EERC is committed to delivering consistent and high-quality research that meets our client's needs and expectations. In order to ensure that the goals of this project are realized, an organizationwide quality management system (QMS), authorized and supported by EERC managers, is in effect and governs all programs within the organization. The EERC established and formalized a QMS and quality control (QC) procedures in August 1988. The *Quality Manual* defines the requirements and the organizational responsibilities for each major element of the QMS and references the supporting documents needed to provide a comprehensive program.

Table 13. Statistical Comparison of the SOH Method to the OH Method

| Run No. | Total Hg | | | Hg ⁰ | | | Hg ²⁺ | | | Particulate-Bound Hg | | |
|---------|-------------------------------------|-------|---------------|-----------------|-------|---------------|------------------|-------|---------------|----------------------|------|---------------|
| | OH | SOH | Diff. | OH | SOH | Diff. | OH | SOH | Diff. | OH | SOH | Diff. |
| 1 | 10.30 | 12.80 | ! 2.50 | 10.10 | 12.80 | ! 2.70 | 0.23 | 0.03 | 0.20 | 0.26 | 0.01 | 0.25 |
| 2 | 10.40 | 16.20 | ! 5.80 | 2.10 | 2.10 | 0.00 | 6.40 | 14.10 | ! 7.70 | 0.38 | 0.08 | 0.30 |
| 3 | 10.90 | 8.10 | 2.80 | 0.54 | 0.58 | ! 0.04 | 8.70 | 7.50 | 1.20 | 0.57 | 0.60 | ! 0.03 |
| 4 | 8.60 | 8.50 | 0.10 | 0.46 | 0.30 | 0.16 | 7.90 | 8.20 | ! 0.30 | 0.30 | 0.10 | 0.20 |
| 5 | 7.70 | 8.30 | ! 0.60 | 0.46 | 0.35 | 0.11 | 6.80 | 7.90 | ! 1.10 | 0.63 | 0.91 | ! 0.28 |
| 6 | 34.40 | 37.20 | ! 2.80 | 5.90 | 4.10 | 1.80 | 28.00 | 32.50 | -4.50 | 6.89 | 3.72 | 3.17 |
| 7 | 35.80 | 33.50 | 2.30 | 6.80 | 7.10 | ! 0.30 | 28.70 | 26.30 | 2.40 | 8.89 | 8.14 | 0.75 |
| 8 | 35.40 | 32.90 | 2.50 | 7.60 | 5.30 | 2.30 | 27.20 | 26.70 | 0.50 | | | |
| 9 | 32.30 | 28.10 | 4.20 | 1.30 | 0.62 | 0.68 | 24.10 | 23.80 | 0.30 | | | |
| 10 | 32.30 | 24.60 | 7.70 | 1.70 | 0.81 | 0.89 | 21.70 | 15.60 | 6.10 | | | |
| 11 | 10.70 | 9.50 | 1.20 | 0.44 | 0.08 | 0.36 | 10.20 | 9.40 | 0.80 | | | |
| 12 | 10.40 | 9.00 | 1.40 | 0.36 | 0.14 | 0.22 | 10.10 | 8.80 | 1.30 | | | |
| 13 | 40.30 | 36.30 | 4.00 | 8.50 | 7.80 | 0.70 | 31.90 | 28.50 | 3.40 | | | |
| 14 | 40.30 | 38.10 | 2.20 | 9.10 | 9.80 | ! 0.70 | 31.10 | 28.30 | 2.80 | | | |
| 15 | 39.00 | 39.50 | ! 0.50 | 9.40 | 9.00 | 0.40 | 29.60 | 30.50 | ! 0.90 | | | |
| 16 | 46.60 | 42.80 | 3.80 | 8.90 | 8.90 | 0.00 | 37.70 | 33.90 | 3.80 | | | |
| | Mean Diff. | | 1.2500 | | | 0.2425 | | | 0.5188 | | | 0.6229 |
| | Mean Std. Dev. | | 3.2490 | | | 1.0826 | | | 3.2486 | | | 1.1667 |
| | Calc. t-Stat. | | 1.5390 | | | 1.4125 | | | 0.8958 | | | 0.6388 |
| | t-Statistic (95% confidence) | | 1.7530 | | | 1.7530 | | | 1.7530 | | | 1.9430 |

Compliance with this manual and its supporting documents ensures that the EERC adequately fulfills governmental and private clients' requirements relating to quality and compliance with applicable regulations, codes, and protocols. This project is required to follow the *Quality Manual*, project-specific quality assurance (QA) procedures, and all revisions. The EERC QA manager implements and oversees all aspects of QA/QC for all research, development, and demonstration projects and will review the QA/QC components of this project. The project manager is responsible for ensuring that project-specific QA/QC protocols are followed.

The EERC maintains a wide range of laboratories and equipment for solid, liquid, and gaseous characterization of the physical, chemical, mineralogical, biological, hydrological, and geological properties of natural and synthetic materials and processes. Laboratory procedures and instrument calibrations follow nationally recognized or approved standards and methods put forth by EPA, ASTM, National Institute of Standards and Technology (NIST), and other agencies. Each laboratory manager is responsible for ensuring that the applicable QA/QC procedures in this project are implemented. It is expected that the strongest QA/QC evaluation of the SPDC tests will be based on

a mercury mass balance calculation. Sufficient QA/QC data will be generated to assess both accuracy and precision of the SPDC data. This includes duplicate samples of total gas- and particulate-phase mercury. The following QA/QC requirements are specific to this project.

7.1 QA/QC for the Ontario Hydro Mercury Speciation Method

All data sheets, volumetric flasks, and petri dishes used for sample recovery were marked with preprinted labels. All labels included identifying data, including date, time, run number, sample port location, and the name of the sampler.

Prior to being used for the sampling, all glassware was washed with hot, soapy water, then rinsed with deionized water three times, soaked in 10% V/V nitric acid for a minimum of 4 hours, rinsed an additional three times with deionized water, and dried. The glassware was then stored in closed containers until it was used.

As part of the QA/QC procedures during the pilot-scale tests, both field blanks and field spikes were completed. The results are shown in Tables 14 and 15. A field blank is to determine if there is any mercury contamination. If the field blank shows contamination above instrument background, steps need to be taken to eliminate or reduce the contamination to below background levels. Field spikes are completed to ensure that adequate levels of accuracy are maintained. These samples are made up independently of the chemist doing the analyses. The spikes are required to be within 15% of the true value. If the values are not within the specified limits, the instrument is recalibrated and the samples reanalyzed. For these tests, with the exception of one sample, and that one was very close, all field spikes gave recoveries of $100\% \pm 15\%$. A much more detailed discussion of QA/QC is presented in the details of the method found at the EPA web site, <http://www.epa.gov/ttn/emc/prelim.html>.

7.2 Quality Control for the SOH Sampling

The following section summarizes QC measures undertaken to ensure that the analysis of the SOH method samples was completed under very good control. The results are summarized in the table which follows and are discussed in the text below. Included in the text is the "data quality objective" or DQO, which is essentially the quality objectives or control limits expected for the results of the SOH method to be considered good.

Table 14. Field Blank Results for OH Method

| Blanks | KCl | H ₂ O ₂ | KMnO ₄ |
|--------|-------|-------------------------------|-------------------|
| 1 | <0.03 | 0.08 | 0.04 |
| 2 | <0.03 | 0.09 | <0.03 |
| 3 | 0.05 | <0.03 | |

Table 15. Field Spike Results for the OH Method

| Solution | Expected, µg/L | Measured, µg/L | Recovery, % |
|-------------------------------|-------------------|-------------------|----------------|
| KMnO ₄ | 10 | 8.80 | 88.0 |
| KMnO ₄ | 10 | 8.55 | 85.5 |
| KMnO ₄ | 10 | 10.15 | 101.2 |
| KCl | 10 | 9.91 | 99.1 |
| KCl | 10 | 10.01 | 100.1 |
| KCl | 10 | 10.40 | 104.0 |
| H ₂ O ₂ | 5.2 | 5.67 | 109.0 |
| H ₂ O ₂ | 2 | 1.66 | 83.0 |
| H ₂ O ₂ | 2 | 2.28 | 114.0 |
| H ₂ O ₂ | 5 | 4.40 | 88.0 |
| H ₂ O ₂ | 10 | 9.95 | 99.5 |
| H ₂ O ₂ | 4.8 | 4.39 | 91.5 |

The results reported below include lab analysis replicates, system blanks, matrix spikes, and standard reference material (SRM) recoveries. QC data are extracted from various sample analysis data sheets. The file names and extensions are included in the table below.

Replicate Analysis. Replicate sample analysis provides the means to measure the precision of the CVAFS analytical method. In most cases, replicate analysis occurred on the same analysis day, using the same instrument. However, in many instances, replicate sample analysis occurred on different days and in some cases with different instruments. For samples analyzed in duplicate ($n = 2$), a relative percent difference (RPD) was calculated as a percentage using the formula:

$$\text{RPD} = \text{absolute value of } [A - B] / \text{average } (A + B)$$

If a sample was analyzed in replicate where $n > 2m$, then a relative standard deviation (RSD) is calculated as a percentage using the following formula where s = standard deviation and m = mean:

$$\text{RSP} = s/m$$

The laboratory replicate data are shown in Table 16 have an average RPD of 2.2%. Therefore, the projected DQO for lab analysis duplicates of $\pm 20\%$ was readily achieved.

Matrix Limits. The sample analysis matrix spike is a measure of laboratory analysis accuracy and is the addition of 1.00-ng standard spike to a bubbler which also includes a sample aliquot. The recovery of the 1.00-ng spike was calculated as a percent recovery using the formula:

$$\% \text{ Recovery} = \frac{(\text{ng/aliquot of the spike} + \text{ng/aliquot of the sample})}{(\text{ng/aliquot of the sample} + 1.00 \text{ ng})}$$

The results of the matrix spike were excellent ($\sigma = 5.7\%$) and are shown in Table 17. Therefore, the DQO for the sample analysis matrix spike of ± 2.5 was always met during this study.

Sample Blanks. The blanks for both the KCl denuders and the SOH traps were all less than 0.1 ng per trap, as shown in Table 18.

8.0 CONCLUSIONS

Based on the SPDC tests, the following conclusions can be made:

- Good mass balances were obtained for the tests, $100 \pm 25\%$.
- The Hg^{2+} and the particulate-bound Hg decrease rapidly to at or near zero.

Table 16. SOH QC Replicate Results

| Sample ID | Rep. 1 | Rep. 2 | Mean | RPD |
|---------------------|--------|--------|-------|------|
| ICA-SOH-7-0307 AD | 389.2 | 395.0 | 392.1 | 1.5% |
| KCLA-SOH-10-0307 AD | 378.9 | 384.6 | 381.7 | 1.5% |
| KCLA-2030800 AD | 177.0 | 180.7 | 178.9 | 2.1% |
| IC-A-11030800 AD | 47.8 | 48.4 | 48.1 | 1.4% |
| KCLB-7031300 AD | 150.3 | 153.4 | 151.8 | 2.0% |
| PHG-2031400 AD | 60.6 | 63.3 | 61.9 | 4.5% |

Table 17. SOH Sample Analysis Matrix Spikes

| Sample ID | Recovery, % |
|------------------------------|----------------|
| ICA-SOH-7-0307 AS + 1.0 ng | 98.0 |
| KCLA-SOH-10-0307 AS + 1.0 ng | 92.8 |
| KCLA-2030800 AS + 1.0 ng | 106.4 |
| IC-A-11030800 AS + 1.0 ng | 107.7 |
| KCLB-7031300 AS + 1.0 ng | 105.0 |
| PHG-2031400 AS + 1.0 ng | 95.5 |
| KCLA-5031500 AS + 1.0 ng | 100.7 |

Table 18. SOH Blanks

| Blank No. | KCl Denuder, ng/trap | SOH Trap, ng/trap |
|----------------------|---------------------------------|------------------------------|
| 1 | 0.0086 | 0.0223 |
| 2 | 0.0020 | 0.0032 |
| 3 | 0.0019 | 0.0105 |
| 4 | 0.0015 | 0.0044 |
| 5 | 0.0010 | 0.0087 |
| 6 | 0.0025 | 0.0069 |
| 7 | 0.0032 | 0.0017 |
| 8 | 0.0068 | 0.0196 |
| 9 | 0.0017 | 0.0836 |
| 10 | 0.0041 | 0.0041 |
| 11 | 0.0014 | 0.0047 |
| Mean | 0.0032 | 0.0154 |
| Std. Dev. | 0.0024 | 0.0236 |

- There was for almost all tests a rapid increase in Hg^0 ; however, not nearly to the degree that the Hg^{2+} and particulate bound-mercury decreased.
- The data appear to indicate that some reduction of Hg^{2+} to Hg^0 does take place in the SPDC (or plume?).
- The size of the SPDC (0.5 m^3) resulted in severe wall effects; a high percentage of the mercury goes to the wall to be removed later by the rinses.
- Because of the very rapid decrease in Hg^{2+} and the particulate-bound Hg, it was not possible to statistically evaluate the effects of light and rain on mercury chemistry in the SPDC.
- Because of the wall effects, a static SPDC is not a very useful tool in understanding mercury chemistry in combustion plumes. However, a dynamic system where flue gas is constantly flowing through the device and mixing with air may eliminate these effects.

Conclusion sampling methodology are as follows:

- The Tekran mercury CEM with KCl denuders appeared to work well in speciating and measuring low levels of mercury.
- The SOH method statistically gave the same results as the Ontario Hydro mercury speciation method.

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APPENDIX A

SPDC DATA

APPENDIX B

A VALIDATION STUDY AT THE EERC OF THE FLUE GAS MERCURY SORBENT SPECIATION OR FMSS METHOD